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KEY CONCEPTS IN TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY

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We give an overview of the underlying concepts of time-dependent density-functional theory. The basic relations between densities, potentials and initial states, for time-dependent many-body systems are discussed. We obtain some new results concerning the invertability of response functions. Some fundamental difficulties associated with the time-dependent action principle are discussed and we show how these difficulties can be resolved by means of the Keldysh formalism.

1. Introduction

A large field of research in physics is concerned with many-electron systems in time-dependent external fields. One could, for instance, think of linear response properties of molecules and solids. In this regime one considers external fields which cause a small perturbation of the initial ground state of the system. Many important physical quantities can be obtained from such a calculation,^{1–3} such as polarizabilities, dielectric functions, excitation energies, photoabsorption spectra, and van der Waals coefficients. Beyond linear response the situation becomes much more complicated. One can for instance think of atoms and molecules in strong laser fields.⁴ A full theoretical description of these systems which involves solving the time-dependent Schrödinger equation is currently beyond computational capabilities and full time-dependent wavefunctions have thusfar only been obtained with large effort and only for small systems⁵ or one-dimensional models.^{6,7} It is therefore clear that new methods must be found to deal in an efficient way with such time-dependent many-particle correlations.

It is therefore worthwhile to explore new methods which deal with time-dependent systems. A promising method is time-dependent density-functional theory (TDDFT).^{8–12} Its most attractive feature is that it transforms the many-body system into a system of noninteracting particles in an effective field. This makes

the method of great practical use. The price we have to pay for transforming the interacting problem to an effective noninteracting one, is that we have to find approximations for the effective field. This effective field is known as the Kohn–Sham potential¹³ and is a functional of the particle density. Its functional dependence on the density is such that the density of the fully interacting system and the effective Kohn–Sham system are identical. Within density functional theory not only the Kohn–Sham potential, but every physical observable is a density functional. The success of density functional theory therefore depends critically on whether or not we can find good approximate density functionals for the quantities of interest. Experience with stationary systems has taught us that in this respect we have been quite fortunate. Already simple approximations such as the local density approximation (LDA) have turned out to be quite successful in the calculation of structures and total energies of molecules and solids.^{14,15} Based on this experience it is therefore interesting to investigate how well density functional theory will perform for time-dependent systems. Calculations within the linear response regime have been very promising^{16–20} and the interest in the field is growing rapidly. It is therefore timely to look back to the foundations of the theory. This article will give an overview of the key concepts underlying time-dependent density functional theory. It is hoped that this work will serve as a basis for further development of more accurate density functionals.

In this paper we first address the question what the time-dependent density can tell us about the dynamics of a many-particle system. We discuss the Runge–Gross theorem²¹ which establishes a one-to-one correspondence between the density and the external potential for a given initial state. The Kohn–Sham construction then forces us to consider different two-particle interactions and initial states. This will lead us to a discussion of the time-dependent v -representability problem.

The most succesful applications of TDDFT are found in the linear response regime. We will give an overview of the properties of the linear response function of the density and establish an invertability proof for a large class of switch-on potentials. The key objects in the response equations of TDDFT are the exchange-correlation potential and its functional derivative, the exchange-correlation kernel. Some basic properties of these quantities are discussed which will hopefully provide some guidelines for the construction of better approximate functionals.

Finally the subtleties related to the action principle are discussed in detail. It is explained why initial derivations of the time-dependent Kohn–Sham equations from a variational principle have lead to paradoxes, and how they can be avoided by the use of functionals that are defined on a so-called Keldysh contour. It is shown how the Keldysh formalism can be used to derive all the equations of TDDFT in a consistent way. The formalism is further illustrated using an exactly solvable model system. Finally we present our conclusions and outlook on future developments within density functional theory.

2. Mapping Between Densities and Potentials

2.1. Ground state density-functional theory by Legendre transforms

In order to study the properties of time-dependent density functionals it is useful to reconsider density functional theory of stationary systems from a different viewpoint than usual. The method described here goes back to the work of De Dominicis and Martin.²² This work discusses the relations between n -body potentials and n -particle density matrices, of which the density-potential relation to be discussed here is a special case. The method will play an important role later, when we will study the action functional for time-dependent density functionals. We consider a Hamiltonian of a stationary many-body system

$$\hat{H}_v = \hat{T} + \hat{V} + \hat{W}, \quad (1)$$

where \hat{T} is the kinetic energy, \hat{V} the external potential, and \hat{W} the two-particle interaction. We denote the Hamilton operator \hat{H}_v with a subindex v to indicate that we will consider the Hamiltonian as a functional of the external potential v . In second quantization the constituent terms are, as usual, written as

$$\hat{T} = -\frac{1}{2} \sum_{\sigma} \int d^3r \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \nabla^2 \hat{\psi}_{\sigma}(\mathbf{r}), \quad (2)$$

$$\hat{V} = \sum_{\sigma} \int d^3r v(\mathbf{r}) \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}), \quad (3)$$

$$\hat{W} = \frac{1}{2} \sum_{\sigma\sigma'} \int d^3r d^3r' w(|\mathbf{r} - \mathbf{r}'|) \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}), \quad (4)$$

where σ and σ' are spin indices. The two-particle potential $w(|\mathbf{r} - \mathbf{r}'|)$ can be arbitrary, but will in practice almost always be equal to the repulsive Coulomb potential. The two-particle interaction is considered to be fixed, whereas the ground state energy $E[v]$ and wavefunction $|\Psi[v]\rangle$ are considered to be functionals of the external potential through solving the time-independent Schrödinger equation

$$(\hat{T} + \hat{V} + \hat{W})|\Psi[v]\rangle = E[v]|\Psi[v]\rangle. \quad (5)$$

From this equation we see that ground state energy as a functional of the external potential v can also be written as

$$E[v] = \langle \Psi[v] | H_v | \Psi[v] \rangle. \quad (6)$$

Our goal is now to go from the potential as our basic variable, to a new variable, which will be the electron density. The deeper reason that this is possible is that the density and the potential are conjugate variables. With this we mean that the contribution of the external potential to the total energy is simply an integral of the potential times the density. We make use of this relation if we take the functional

derivative of the energy functional $E[v]$ with respect to the potential v :

$$\begin{aligned}\frac{\delta E}{\delta v(\mathbf{r})} &= \left\langle \frac{\delta \Psi}{\delta v(\mathbf{r})} \left| H_v \right| \Psi \right\rangle + \langle \Psi | H_v \left| \frac{\delta \Psi}{\delta v(\mathbf{r})} \right\rangle + \langle \Psi | \frac{\delta H_v}{\delta v(\mathbf{r})} | \Psi \rangle \\ &= E[v] \frac{\delta}{\delta v(\mathbf{r})} \langle \Psi | \Psi \rangle + \langle \Psi | \sum_{\sigma} \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) | \Psi \rangle \\ &= \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle = n(\mathbf{r})\end{aligned}\quad (7)$$

where we used the Schrödinger equation $H_v|\Psi\rangle = E[v]|\Psi\rangle$ and the normalization condition $\langle \Psi | \Psi \rangle = 1$. We further defined the density operator

$$\hat{n}(\mathbf{r}) = \sum_{\sigma} \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}). \quad (8)$$

Note that the equation above is nothing but a functional generalization of the well-known Hellmann–Feynman theorem.²³ Now we can go to the density as our basic variable by defining a Legendre transform

$$F[n] = E[v] - \int d^3r n(\mathbf{r})v(\mathbf{r}) = \langle \Psi[v] | \hat{T} + \hat{W} | \Psi[v] \rangle \quad (9)$$

where v must now be regarded as a functional of n . The uniqueness of such a mapping is guaranteed by the Hohenberg–Kohn theorem.²⁴ The set of densities for which the functional $F[n]$ is defined is the set of so-called v -representable densities. These are ground state densities for a Hamiltonian with external potential v . The question which constraints one has to put on a density to make sure that it is v -representable is known as the v -representability problem. We refer to the literature for more extensive discussions on this point.^{25,26} From $\delta E/\delta v = n$ it follows immediately that

$$\frac{\delta F}{\delta n(\mathbf{r})} = -v(\mathbf{r}). \quad (10)$$

This is our first basic relation. As a remark we note that if we fix the potential v in the Hamiltonian of Eq. (6) we obtain a relation which is more common in textbooks on density-functional theory, namely $\delta E/\delta v = 0$. However, the present approach is more suitable for the extension to the time-dependent case.

In order to derive the Kohn–Sham equations we define the following energy functional for a system of noninteracting particles with external potential v_s and with ground state wavefunction $|\Phi[v_s]\rangle$:

$$E_s[v_s] = \langle \Phi[v_s] | \hat{T} + \hat{V}_s | \Phi[v_s] \rangle \quad (11)$$

with Legendre transform

$$F_s[n] = E[v_s] - \int d^3r n(\mathbf{r})v_s(\mathbf{r}) = \langle \Phi[v_s] | \hat{T} | \Phi[v_s] \rangle, \quad (12)$$

and derivatives

$$\frac{\delta E_s}{\delta v_s(\mathbf{r})} = n(\mathbf{r}), \quad (13)$$

$$\frac{\delta F_s}{\delta n(\mathbf{r})} = -v_s(\mathbf{r}). \quad (14)$$

Finally we define the exchange-correlation functional $E_{xc}[n]$ by the equation

$$F[n] = F_s[n] + \frac{1}{2} \int d^3r d^3r' n(\mathbf{r})n(\mathbf{r}')w(|\mathbf{r} - \mathbf{r}'|) + E_{xc}[n]. \quad (15)$$

This equation assumes that the functionals $F[n]$ and $F_s[n]$ are defined on the same domain of densities. In other words we assume that for a given ground state density of an interacting system there is a noninteracting system with the same density. In other words, we assume that the interacting density is noninteracting- v -representable. If we differentiate Eq. (15) with respect to the density n we obtain

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \int d^3r' n(\mathbf{r}')w(|\mathbf{r} - \mathbf{r}'|) + v_{xc}(\mathbf{r}), \quad (16)$$

where

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \quad (17)$$

is the exchange-correlation potential. Now the state $|\Phi[v_s]\rangle$ is a ground state for a system of noninteracting particles, and can therefore be written as an antisymmetrized product of single-particle orbitals $\varphi_i(\mathbf{r})$. If we now collect our results we see that we have converted the ground state problem into the following set of equations

$$E[v] = \sum_{i=1}^N -\frac{1}{2} \int \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}) + \int d^3r n(\mathbf{r})v(\mathbf{r}) + \frac{1}{2} \int n(\mathbf{r})n(\mathbf{r}')w(|\mathbf{r} - \mathbf{r}'|) + E_{xc}[n], \quad (18)$$

$$\times \left[-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \int d^3r' n(\mathbf{r}')w(|\mathbf{r} - \mathbf{r}'|) + v_{xc}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}), \quad (19)$$

$$n(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2. \quad (20)$$

The above equations constitute the ground state Kohn–Sham equations. These equations turn out to be of great practical use. If we can find a good approximation for the exchange-correlation energy, we can calculate the exchange-correlation potential v_{xc} and solve the orbital equations self-consistently. The density we find in this way can then be used to calculate the ground state energy of the system.

This procedure has been applied with great success for a large range of electronic systems, ranging from molecules to solids.

However, in this work we are interested in time-dependent problems. Let us therefore see if we can generalize the previous derivation to the case that we have a time-dependent perturbing field. This will be the subject of the next section.

2.2. *Some preliminary thoughts on time-dependent density functionals*

In the previous section we arrived in a rather quick fashion at the Kohn–Sham equations. One might therefore think one could do a similar procedure for time-dependent systems. However, we will see that here some problems will arise. We consider the case where we have a time-dependent external field $v(\mathbf{r}t)$ which is described by the following potential energy operator in the Hamiltonian:

$$\hat{V}(t) = \int d^3r v(\mathbf{r}t) \hat{n}(\mathbf{r}). \quad (21)$$

This system will have a time-dependent density $n(\mathbf{r}t)$. In analogy with the previous section it seems natural that we should look for functionals $\tilde{A}[v]$ and $A[n]$ having the property

$$\frac{\delta \tilde{A}}{\delta v(\mathbf{r}t)} = n(\mathbf{r}t), \quad (22)$$

$$\frac{\delta A}{\delta n(\mathbf{r}t)} = v(\mathbf{r}t), \quad (23)$$

and which are related by the Legendre transform

$$A[n] = -\tilde{A}[v] + \int d^3r dt n(\mathbf{r}t) v(\mathbf{r}t). \quad (24)$$

Note that in Eq. (23) we have introduced a relative minus sign compared to Eq. (10) of the stationary case. The functional $F[n]$ for stationary systems should therefore be compared to the functional $-A[n]$ in the time-dependent case.

If we now define functionals $\tilde{A}_s[v_s]$ and $A_s[n]$ for a noninteracting system with external field $v_s(\mathbf{r}t)$ and density $n(\mathbf{r}t)$ and properties

$$\frac{\delta \tilde{A}_s}{\delta v_s(\mathbf{r}t)} = n(\mathbf{r}t), \quad (25)$$

$$\frac{\delta A_s}{\delta n(\mathbf{r}t)} = v_s(\mathbf{r}t), \quad (26)$$

we can easily construct Kohn–Sham equations. For this purpose we define an exchange-correlation functional $A_{xc}[n]$ by

$$A[n] = A_s[n] - \frac{1}{2} \int d^3r d^3r' dt n(\mathbf{r}t) n(\mathbf{r}'t) w(|\mathbf{r} - \mathbf{r}'|) - A_{xc}[n]. \quad (27)$$

Differentiation of this equation with respect to $n(\mathbf{r}t)$ then yields

$$v_s(\mathbf{r}t) = v(\mathbf{r}t) + \int d^3r' n(\mathbf{r}'t) w(|\mathbf{r} - \mathbf{r}'|) + v_{xc}(\mathbf{r}t) \quad (28)$$

where

$$v_{xc}(\mathbf{r}t) = \frac{\delta A_{xc}}{\delta n(\mathbf{r}t)} \quad (29)$$

is the time-dependent exchange-correlation potential. Since $v_s(\mathbf{r}t)$ is the external potential for a noninteracting system with density $n(\mathbf{r}t)$, we obtain the time-dependent Kohn–Sham equations²¹

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}t) + \int d^3r' n(\mathbf{r}'t) w(|\mathbf{r} - \mathbf{r}'|) + v_{xc}(\mathbf{r}t) \right] \varphi_i(\mathbf{r}t) = i\partial_t \varphi_i(\mathbf{r}t), \quad (30)$$

$$n(\mathbf{r}t) = \sum_{i=1}^N |\varphi_i(\mathbf{r}t)|^2. \quad (31)$$

This derivation seems straightforward enough. We only have to find an explicit definition of our starting functional $\tilde{A}[v]$ in terms of the Hamiltonian. It is exactly here that a major problem arises. The problem is that one can not find a functional $\tilde{A}[v]$ with the property

$$n(\mathbf{r}t) = \frac{\delta \tilde{A}}{\delta v(\mathbf{r}t)}. \quad (32)$$

The reason is that this equation would imply that

$$\frac{\delta^2 \tilde{A}}{\delta v(\mathbf{r}t) \delta v(\mathbf{r}'t')} = \frac{\delta n(\mathbf{r}t)}{\delta v(\mathbf{r}'t')}. \quad (33)$$

Now the left hand side of this equation is symmetric in the space-time arguments, whereas the right hand side of this equation is the density response function which has a causal structure, i.e. it is zero for $t' > t$. Therefore the causality and symmetry requirements contradict each other.^{10,11,27} We conclude that there is no differentiable functional of the external field with property (32). Consequently there is also no functional of the density with the property $\delta A/\delta n = v$ (otherwise we could construct a functional \tilde{A} with property (32) by means of a Legendre transform). The same is, of course, true for the noninteracting functionals $\tilde{A}_s[v_s]$ and $A_s[n]$. We therefore conclude that the Kohn–Sham potential can not be obtained as a functional derivative with respect to the density. We note, however, that a Kohn–Sham potential can still be defined as that potential $v_s[n]$, that, in a noninteracting system, yields a given density $n(\mathbf{r}t)$. This definition of the Kohn–Sham potential is based on a one-to-one mapping between densities and potentials that can be proven directly from the time-dependent Schrödinger equation. On the basis of this mapping we can therefore still define time-dependent Kohn–Sham equations. However, in this way we have lost a connection between action functionals and potentials. Such a connection can be useful for the derivation of new approximate potentials.

This difficulty is resolved later when we will show that the Kohn–Sham potential can still be obtained as a functional derivative of an extended type of action functional defined on a new time contour.

2.3. Local conservation laws

Before we discuss some other properties of density functionals we will first describe some general properties of time-dependent many-body systems. The relations derived will be used later in some basic proofs of time-dependent density functional theory.

We consider systems in which the time-dependent external field can be described by a time-dependent scalar potential $v(\mathbf{r}t)$. We start from a Hamiltonian \hat{H} of a finite many-particle system

$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{W}, \quad (34)$$

where \hat{T} is the kinetic energy, $\hat{V}(t)$ the external potential, and \hat{W} the two-particle interaction. The explicit forms of these terms have been defined before. The whole time-dependent dynamics of the system is given by the solution of the time-dependent Schrödinger equation:

$$(i\partial_t - \hat{H}(t))|\Psi(t)\rangle = 0 \quad (35)$$

with the initial condition $|\Psi(t_0)\rangle = |\Psi_0\rangle$. This is therefore an initial value problem for which we need to specify an initial state. A commonly occurring initial value problem is one where we consider a system which is in the ground state before a certain time t_0 . For $t > t_0$ the system is then perturbed by an external field and we are interested in the response of the system. If the perturbation is weak the problem may be solved by linear response theory. For strong field cases we have to face the full time-dependent problem. The full time-dependent wavefunction is, even for small atoms, a complicated object. Fortunately, some insight can be gained from the consideration of conservation laws of particle number and momentum. The local forms of these conservation laws reduce to relations between densities, currents and the external fields, and can therefore give some information on the structure of density functionals.

The time-dependent density is given as the expectation value of the density operator with the time-dependent many-body wavefunction:

$$n(\mathbf{r}t) = \langle \Psi(t) | \hat{n}(\mathbf{r}) | \Psi(t) \rangle. \quad (36)$$

In the following we consider two continuity equations. If $|\Psi(t)\rangle$ is the state evolving from $|\Psi_0\rangle$ under the influence of Hamiltonian $\hat{H}(t)$ we have the usual continuity equation

$$\partial_t n(\mathbf{r}t) = -i \langle \Psi(t) | [\hat{n}(\mathbf{r}), \hat{H}(t)] | \Psi(t) \rangle = -\nabla \cdot \mathbf{j}(\mathbf{r}t), \quad (37)$$

where the current operator is defined as

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2i} \sum_{\sigma} [\hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \nabla \hat{\psi}_{\sigma}(\mathbf{r}) - (\nabla \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r})) \hat{\psi}_{\sigma}(\mathbf{r})] \quad (38)$$

and has expectation value

$$\mathbf{j}(\mathbf{r}t) = \langle \Psi(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Psi(t) \rangle. \quad (39)$$

This continuity equation expresses, in a local form, the conservation of particle number. Using Gauss' law the continuity equation it simply says that the change of the number of particles within some volume can simply be measured by calculating the flux of the current through the surface of this volume.

As a next step, we can consider an analogous continuity equation for the current itself. We have

$$\partial_t \mathbf{j}(\mathbf{r}t) = -i \langle \Psi(t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)] | \Psi(t) \rangle. \quad (40)$$

If we work out this equation in more detail, we find the expression

$$\partial_t j_k(\mathbf{r}t) = -n(\mathbf{r}t) \partial_k v(\mathbf{r}t) - \sum_i \partial_i T_{ik}(\mathbf{r}t) - W_k(\mathbf{r}t). \quad (41)$$

Here we have defined the momentum-stress tensor (part of the energy-momentum tensor) as

$$\hat{T}_{ik}(\mathbf{r}) = \frac{1}{2} \sum_{\sigma} \left[\partial_i \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \partial_k \hat{\psi}_{\sigma}(\mathbf{r}) + \partial_k \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \partial_i \hat{\psi}_{\sigma}(\mathbf{r}) - \frac{1}{2} \partial_i \partial_k (\hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r})) \right] \quad (42)$$

and the quantity \hat{W}_k as

$$\hat{W}_k(\mathbf{r}) = \sum_{\sigma, \sigma'} \int d^3 r' \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}') \partial_k w(|\mathbf{r} - \mathbf{r}'|) \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}), \quad (43)$$

where the derivative ∂_k is taken with respect to the variable \mathbf{r} . Their expectation values are defined as

$$T_{ik}(\mathbf{r}t) = \langle \Psi(t) | \hat{T}_{ik} | \Psi(t) \rangle, \quad (44)$$

$$W_k(\mathbf{r}t) = \langle \Psi(t) | \hat{W}_k | \Psi(t) \rangle. \quad (45)$$

The continuity equation (41) is a local quantum version of Newton's third law. This is readily seen by integrating this equation over space. In that case the term with the stress-momentum tensor disappears since it is a total derivative (assuming that T_{ik} vanishes sufficiently fast at infinity). The integral over W_k disappears too:

$$\int d^3 r W_k(\mathbf{r}t) = \int d^3 r d^3 r' \Gamma(\mathbf{r}, \mathbf{r}', t) \partial_k w(|\mathbf{r} - \mathbf{r}'|) = 0, \quad (46)$$

where we defined the diagonal two-particle density matrix as

$$\Gamma(\mathbf{r}, \mathbf{r}', t) = \langle \Psi(t) | \sum_{\sigma, \sigma'} \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}) | \Psi(t) \rangle. \quad (47)$$

This follows because Γ is a symmetric function of the variables \mathbf{r} and \mathbf{r}' whereas $\partial_k w(|\mathbf{r} - \mathbf{r}'|)$ is an odd function. We therefore find that integration of Eq. (41) yields

$$\partial_t \mathbf{P}(t) = \int d^3 r \partial_t \mathbf{j}(\mathbf{r}t) = - \int d^3 r' n(\mathbf{r}t) \nabla v(\mathbf{r}t), \quad (48)$$

where we defined the momentum of the system by

$$\mathbf{P}(t) = \int d^3 r \mathbf{j}(\mathbf{r}t). \quad (49)$$

Equation (48) states that the change of momentum of a system is equal to the force on that system. In other words, this is Newton's third law. As a side remark we may further mention that the local form of Newton's third law also has been studied in connection with many-body perturbation theory, in particular concerning so-called conserving approximations.²⁸⁻³⁰

Let us finally consider the angular momentum of the system, defined as

$$\mathbf{L}(t) = \int d^3 r \mathbf{r} \times \mathbf{j}(\mathbf{r}t). \quad (50)$$

If we take the time-derivative of this equation and use the continuity equation we obtain

$$\begin{aligned} \partial_t L_i(t) &= \int d^3 r (\mathbf{r} \times \partial_t \mathbf{j}(\mathbf{r}t))_i \\ &= \sum_{ijk} \int d^3 r \epsilon_{ijk} r_j \left(-n(\mathbf{r}t) \partial_k v(\mathbf{r}t) - \sum_l \partial_l T_{lk}(\mathbf{r}t) - W_k(\mathbf{r}t) \right), \end{aligned} \quad (51)$$

where ϵ_{ijk} is the anti-symmetric Levi-Civita tensor which assumes the values 1 and -1 for respectively even and odd permutations of the indices. This can be rewritten as

$$\begin{aligned} \partial_t L_i(t) &= - \int d^3 r (\mathbf{r} \times \nabla v(\mathbf{r}t))_i + \sum_{jk} \int d^3 r \epsilon_{ijk} T_{jk} \\ &\quad + \int d^3 r d^3 r' (\mathbf{r} \times \mathbf{r}')_i \Gamma(\mathbf{r}, \mathbf{r}', t) \frac{1}{\rho} \frac{\partial w}{\partial \rho}, \end{aligned} \quad (52)$$

where we defined $\rho = |\mathbf{r} - \mathbf{r}'|$ and in the second term performed a partial integration where we used $\partial_l r_j = \delta_{lj}$. Now the second term disappears since T_{jk} is a symmetric tensor contracted with the antisymmetric ϵ_{ijk} tensor. The last term disappears too, since $\Gamma(\mathbf{r}, \mathbf{r}', t)$ is symmetric in \mathbf{r} and \mathbf{r}' , whereas $\mathbf{r} \times \mathbf{r}'$ is antisymmetric. Note that we explicitly used that the two-particle interaction depends on $|\mathbf{r} - \mathbf{r}'|$. Collecting our results we obtain

$$\partial_t \mathbf{L}(t) = \int d^3 r \mathbf{r} \times \partial_t \mathbf{j}(\mathbf{r}t) = - \int d^3 r n(\mathbf{r}t) \mathbf{r} \times \nabla v(\mathbf{r}t). \quad (53)$$

This equation therefore tells us that the time-derivative of the angular momentum is equal to the torque due to the external field acting on the system.

We further mention a relation which we will need later in our discussion. Taking the divergence of Eq. (41) and using the continuity Eq. (37) we find

$$\partial_t^2 n(\mathbf{r}t) = \nabla \cdot (n(\mathbf{r}t) \nabla v(\mathbf{r}t)) + q(\mathbf{r}t) \quad (54)$$

with $q(\mathbf{r}t)$ being defined as the expectation value

$$q(\mathbf{r}t) = \langle \Psi(t) | \hat{q}(\mathbf{r}) | \Psi(t) \rangle \quad (55)$$

and where the operator $\hat{q}(\mathbf{r})$ is given by

$$\hat{q}(\mathbf{r}) = \sum_{i,k} \partial_i \partial_k \hat{T}_{ik}(\mathbf{r}) + \sum_k \partial_k \hat{W}_k(\mathbf{r}). \quad (56)$$

Equation (54) will play a central role in our discussion of the relation between the density and the potential. This is because it represents an equation which directly relates the external potential and the electron density.

2.4. The Runge–Gross proof

We will now investigate a basic relation between the external potential and the time-dependent density. Such a relation has been investigated by Runge and Gross and the main result of this work is known as the Runge–Gross theorem.²¹ This theorem states that two densities $n(\mathbf{r}t)$ and $n'(\mathbf{r}t)$ evolving from a common initial state $|\Psi_0\rangle$ under the influence of two potentials $v(\mathbf{r}t)$ and $v'(\mathbf{r}t)$ (which are both assumed to have a Taylor expansion around the initial time t_0) are always different provided that the potentials differ by more than a purely time-dependent (\mathbf{r} -independent) function:

$$v(\mathbf{r}t) \neq v'(\mathbf{r}t) + C(t). \quad (57)$$

The proof of this theorem consists of two steps. In the first step one shows that the current densities $\mathbf{j}(\mathbf{r}t)$ and $\mathbf{j}'(\mathbf{r}t)$ corresponding to the systems with potential $v(\mathbf{r}t)$ and $v'(\mathbf{r}t)$ will differ. To show this we first use the condition that the potentials $v(\mathbf{r}t)$ and $v'(\mathbf{r}t)$ can be expanded in a Taylor series:

$$v(\mathbf{r}t) = \sum_{k=0} \frac{1}{k!} v_k(\mathbf{r})(t - t_0)^k. \quad (58)$$

We have a similar equation for $v'(\mathbf{r}t)$ with coefficients $v'_k(\mathbf{r})$. Equation (57) is equivalent to the statement that, given the expansion coefficients $v_k(\mathbf{r})$ and $v'_k(\mathbf{r})$, there exists a smallest integer $k \geq 0$ such that

$$w_k(\mathbf{r}) = v_k(\mathbf{r}) - v'_k(\mathbf{r}) \neq \text{constant}. \quad (59)$$

If we use the quantum mechanical equation of motion for a Schrödinger operator $\hat{A}(t)$,

$$\partial_t \langle \Psi(t) | \hat{A}(t) | \Psi(t) \rangle = \langle \Psi(t) | \partial_t \hat{A}(t) - i[\hat{A}(t), \hat{H}(t)] | \Psi(t) \rangle, \quad (60)$$

we obtain for the current densities:

$$\begin{aligned}\partial_t(\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t))|_{t=t_0} &= -i\langle\Psi_0|[\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t_0) - \hat{H}'(t_0)]|\Psi_0\rangle \\ &= -n_0(\mathbf{r})\nabla(v(\mathbf{r}t_0) - v'(\mathbf{r}t_0))\end{aligned}\quad (61)$$

where $n_0(\mathbf{r}) = n(\mathbf{r}t_0)$ is the initial density. If condition (59) is satisfied for $k = 0$ then the currents $\mathbf{j}(\mathbf{r}t)$ and $\mathbf{j}'(\mathbf{r}t)$ will become different infinitesimally later than t_0 . It could still be that $w_k(\mathbf{r})$ is constant for $k = 0$ in Eq. (59) and in that case the initial time-derivatives of the currents are equal. However, there must always be a smallest k such that $w_k(\mathbf{r})$ is not constant. If we then use Eq. (60) $(k+1)$ times we obtain:

$$\partial_t^{k+1}(\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t))|_{t=t_0} = -n_0(\mathbf{r})\nabla w_k(\mathbf{r}) \neq 0. \quad (62)$$

We can therefore conclude that $\mathbf{j}(\mathbf{r}t) \neq \mathbf{j}'(\mathbf{r}t)$. To prove a similar statement for the densities we use the continuity equation

$$\partial_t(n(\mathbf{r}t) - n'(\mathbf{r}t)) = -\nabla \cdot (\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t)). \quad (63)$$

The $(k+1)$ th time-derivative of this equation then yields

$$\partial_t^{k+2}(n(\mathbf{r}t) - n'(\mathbf{r}t))|_{t=t_0} = \nabla \cdot (n_0(\mathbf{r})\nabla w_k(\mathbf{r})). \quad (64)$$

If we want to prove that $n(\mathbf{r}t)$ and $n'(\mathbf{r}t)$ will become different for times $t > t_0$ we have to show that the right hand side of Eq. (64) can not vanish identically. For this we note that

$$\begin{aligned}\int d^3r n_0(\mathbf{r})(\nabla w_k(\mathbf{r}))^2 &= -\int d^3r w_k(\mathbf{r})\nabla \cdot (n_0(\mathbf{r})\nabla w_k(\mathbf{r})) \\ &+ \oint d\mathbf{S} \cdot (n_0(\mathbf{r})w_k(\mathbf{r})\nabla w_k(\mathbf{r}))\end{aligned}\quad (65)$$

where we have used Green's theorem. For physically realistic potentials (i.e. potentials that arise from normalizable external charge densities) the surface integral vanishes, because for such potentials the quantities $w_k(\mathbf{r})$ fall off at least as fast as $1/r$ while the density itself decays exponentially. Therefore $\nabla \cdot (n_0\nabla w_k(\mathbf{r})) \neq 0$ because that would imply that the left hand side of Eq. (65) is zero. This in turn would imply that $(\nabla w_k(\mathbf{r}))^2 = 0$ which is in contradiction to the assumption that $w_k(\mathbf{r})$ is not constant. This completes the proof of the theorem.

There is another important observation to be made from this proof. In Eq. (64) the density difference $n(\mathbf{r}t) - n'(\mathbf{r}t)$ is linear in $w_k(\mathbf{r})$. This density difference is therefore nonvanishing already to first order in $v(\mathbf{r}t) - v'(\mathbf{r}t)$. This means in particular that the linear density response function is invertible for switch-on processes.

2.5. Extension to different interactions and initial states

In the previous section we concluded that for a given initial state the time-dependent density is a unique functional of the external potential. Let us elaborate a bit further

on this point. Suppose we could solve the time-dependent Schrödinger equation for a given many-body system, i.e. we specify an initial state $|\Psi_0\rangle$ at $t = t_0$ and evolve the wavefunction in time using the Hamiltonian $\hat{H}(t)$. Then, from the wavefunction, we can calculate the time-dependent density $n(\mathbf{r}t)$. We can then ask ourselves the following question:

Can exactly the same density $n(\mathbf{r}t)$ be reproduced by an external potential $v'(\mathbf{r}t)$ in a system with a different given initial state and a different two-particle interaction, and if so, would this potential be unique (modulo a purely time-dependent function)?

The answer to this question is obviously of great importance for the construction of the time-dependent Kohn–Sham equations. The Kohn–Sham system has no two-particle interaction and differs in this respect from the fully interacting system. It has, in general, also a different initial state. This state is usually a Slater determinant rather than a fully interacting initial state. A time-dependent Kohn–Sham system therefore only exists if the question posed above can be answered affirmatively. We will show in the following, that with some restrictions on the initial states and potentials, this question can indeed be answered affirmatively.³¹

We proceed carefully by first restricting ourselves to external potentials $v(\mathbf{r}t)$ that are of the form

$$v(\mathbf{r}t) = \int d^3r' \frac{Z(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|}, \quad (66)$$

where $Z(\mathbf{r}t)$ describes a finite but arbitrarily large charge distribution. The external potential is thus assumed to be generated by some finite, and in general time-dependent, charge distribution. This form is chosen to make the integrals in our discussion well-defined. However, the form is not particularly restrictive as it encompasses most cases of physical interest. For instance, if $Z(\mathbf{r}t)$ is a delta-function-like distribution of point charges then $v(\mathbf{r}t)$ describes a molecular framework. The form Eq. (66) excludes some commonly used external fields, such as the potential of a spatially homogeneous electric field. However, for practical purposes, these fields can always be approximated to arbitrary accuracy by considering very large but finite charge distributions (which is actually closer to the real physical situation). We further assume $v(\mathbf{r}t)$ to be an analytic function of time t , i.e. $v(\mathbf{r}t)$ must have a Taylor expansion with finite convergence radius for each time t .

Let us now assume that we have solved the time-dependent Schrödinger equation for the many-body system described by Hamiltonian $\hat{H}(t)$ and initial state $|\Psi_0\rangle$ at $t = t_0$. We then have obtained a many-body wavefunction $|\Psi(t)\rangle$ and density $n(\mathbf{r}t)$. As shown before in section 2.3 this density satisfies the equation

$$\partial_t^2 n(\mathbf{r}t) = \nabla \cdot (n(\mathbf{r}t) \nabla v(\mathbf{r}t)) + q(\mathbf{r}t), \quad (67)$$

where $q(\mathbf{r}t)$ is defined in Eqs. (55) and (56). We now consider a second system with Hamiltonian

$$\hat{H}'(t) = \hat{T} + \hat{V}'(t) + \hat{W}'. \quad (68)$$

The terms $\hat{V}'(t)$ and \hat{W}' represent again the one- and two-body potentials. We denote the initial state by $|\Phi_0\rangle$ at $t = t_0$ and time-evolved state by $|\Phi(t)\rangle$. The form of \hat{W}' is assumed to be such that $\hat{W}'_k(\mathbf{r}t)$ and its derivatives are finite. For the most important case of interest, i.e. $\hat{W}' = \lambda\hat{W}$ with $0 \leq \lambda \leq 1$, this is automatically satisfied. We will discuss some special cases of this type later on. For the system described by Hamiltonian \hat{H}' we have an equation analogous to Eq. (54). Assuming that the other system has identical density, i.e. $n'(\mathbf{r}t) = n(\mathbf{r}t)$, we have

$$\partial_t^2 n(\mathbf{r}t) = \nabla \cdot (n(\mathbf{r}t) \nabla v'(\mathbf{r}t)) + q'(\mathbf{r}t), \quad (69)$$

where $q'(\mathbf{r}t)$ is the expectation value

$$q'(\mathbf{r}t) = \langle \Phi(t) | \hat{q}'(\mathbf{r}) | \Phi(t) \rangle, \quad (70)$$

for which we defined

$$\hat{q}' = \sum_{i,k} \partial_i \partial_k \hat{T}_{ik}(\mathbf{r}) + \sum_k \partial_k \hat{W}'_k(\mathbf{r}). \quad (71)$$

By subtracting Eqs. (54) and (69) we find

$$\nabla \cdot (n(\mathbf{r}t) \nabla \omega(\mathbf{r}t)) = \zeta(\mathbf{r}t), \quad (72)$$

where $\omega(\mathbf{r}t) = v(\mathbf{r}t) - v'(\mathbf{r}t)$ and $\zeta(\mathbf{r}t) = q'(\mathbf{r}t) - q(\mathbf{r}t)$. Equation (72) is the equation we will use to construct $v'(\mathbf{r}t)$. First we need to discuss some initial and boundary conditions. As a necessary condition for the potential v' to exist, we have to require that the initial states $|\Psi_0\rangle$ and $|\Phi_0\rangle$ yield the same initial density, i.e.

$$\langle \Phi_0 | \hat{n}(\mathbf{r}) | \Phi_0 \rangle = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle. \quad (73)$$

We now note that the basic equation (54) is a second order differential equation in time for $n(\mathbf{r}t)$. This means that we still need as additional requirement that $\partial_t n'(\mathbf{r}t) = \partial_t n(\mathbf{r}t)$ at $t = t_0$. With help of the continuity equation (37) this yields the condition

$$\langle \Phi_0 | \nabla \cdot \hat{\mathbf{j}}(\mathbf{r}) | \Phi_0 \rangle = \langle \Psi_0 | \nabla \cdot \hat{\mathbf{j}}(\mathbf{r}) | \Psi_0 \rangle. \quad (74)$$

This constraint also implies the weaker requirement that the initial state $|\Phi_0\rangle$ must be chosen in such a way that the initial linear momenta $\mathbf{P}(t_0)$ of both systems are the same. This follows directly from the fact that the momentum of the system is given by

$$\mathbf{P}(t) = \int d^3r \mathbf{j}(\mathbf{r}t) = \int d^3r r \partial_t n(\mathbf{r}t). \quad (75)$$

The equality of the last two terms in this equation follows directly from the continuity equation (37) and the fact that we are dealing with finite systems for which, barring pathological examples, currents and densities are zero at infinity (see below and Appendix). This also helps us to understand the physics behind constraint (74). If the densities of both systems described by Hamiltonian \hat{H} and \hat{H}' are the same at all times then the above Eq. (75) implies that also the momenta of both systems

are equal at all times. This clearly can not be satisfied if the initial momenta of both systems are different, since it would require an infinite force to make them equal for $t > t_0$.

It turns out (see Appendix), however, that one can construct examples of initial states for a finite system that satisfy constraint (73) and constraint (74), but for which the current at infinity does not vanish.³² These initial states will have an infinite momentum and kinetic energy expectation value. We want to exclude these pathological cases by putting a third constraint on the initial state:

$$\mathbf{P}(t_0) = \int d^3r \langle \Phi_0 | \hat{\mathbf{j}}(\mathbf{r}) | \Phi_0 \rangle < \infty \quad (76)$$

i.e. we require that the state $|\Phi_0\rangle$ has a finite initial momentum, which then by Eq. (75) coincides with the initial momentum of state $|\Psi_0\rangle$. With the initial conditions Eq. (73) and Eq. (74) and Eq. (76), we now discuss the solution of Eq. (72). We first notice that this equation contains no time-derivatives and the time-variable can therefore be treated as a parameter. We further notice that this equation is of a well-known Sturm–Liouville type, which has a unique solution for $\omega(\mathbf{r}t)$ if $n(\mathbf{r}t)$ and $\zeta(\mathbf{r}t)$ are given and if we further specify as boundary condition that $\omega(\mathbf{r}t)$ approaches zero at infinity (for further details on this point we refer to the Appendix). Imposing the latter boundary condition at infinity also means that we choose a particular gauge for the potential $v'(\mathbf{r}t)$, i.e. we fix the arbitrary time-dependent function $C(t)$ mentioned above. Note that this boundary condition at infinity is also satisfied for the potential $v(\mathbf{r}t)$ of Eq. (66). At $t = t_0$ we have

$$\nabla \cdot (n(\mathbf{r}t_0) \nabla \omega(\mathbf{r}t_0)) = \zeta(\mathbf{r}t_0). \quad (77)$$

Since $n(\mathbf{r}t)$ is known at all times and since $\zeta(\mathbf{r}t_0)$ can be calculated from the initial states $|\Psi_0\rangle$ and $|\Phi_0\rangle$ there is a unique solution $\omega(\mathbf{r}t_0)$, provided we take into account the boundary condition. This means that we have determined $v'(\mathbf{r}t_0) = v(\mathbf{r}t_0) - \omega(\mathbf{r}t_0)$. In the next step we take the time-derivative of Eq. (72) at $t = t_0$ and obtain

$$\nabla \cdot (n(\mathbf{r}t_0) \nabla \omega^{(1)}(\mathbf{r})) = \zeta^{(1)}(\mathbf{r}) - \nabla \cdot (n^{(1)}(\mathbf{r}) \nabla \omega(\mathbf{r}t_0)), \quad (78)$$

where we introduced the following notation for the k th time-derivative at $t = t_0$:

$$f^{(k)}(\mathbf{r}) = \partial_t^k f(\mathbf{r}t)|_{t=t_0}. \quad (79)$$

Now all quantities on the right hand side of Eq. (78) are known, since $n(\mathbf{r}t)$ is known at all times and $\omega(\mathbf{r}t_0)$ was already determined from Eq. (77). The quantity $\zeta^{(1)}(\mathbf{r})$ is calculated from the commutators:

$$\zeta^{(1)}(\mathbf{r}) = \partial_t \zeta(\mathbf{r}t)|_{t=t_0} = i \langle \Psi_0 | [\hat{q}(\mathbf{r}), \hat{H}(t_0)] | \Psi_0 \rangle - i \langle \Phi_0 | [\hat{q}'(\mathbf{r}), \hat{H}'(t_0)] | \Phi_0 \rangle, \quad (80)$$

where $\hat{H}'(t_0)$ is known from our previous calculation of $v'(\mathbf{r}t_0)$. From Eq. (78), which is of the same Sturm–Liouville type as Eq. (77), we can therefore calculate $\omega^{(1)}(\mathbf{r})$ (using the same boundary condition at infinity as before) and hence we get $\partial_t v'(\mathbf{r}t)$ at $t = t_0$. By taking the second time derivative of Eq. (72) we can repeat

the above procedure and obtain $\partial_t^2 v'(\mathbf{r}t)$ at $t = t_0$. In general, if we take the k th time derivative of Eq. (72), we obtain

$$\nabla \cdot (n(\mathbf{r}t_0) \nabla \omega^{(k)}(\mathbf{r})) = Q^{(k)}(\mathbf{r}), \quad (81)$$

where the inhomogeneity $Q^{(k)}(\mathbf{r})$ is given by

$$Q^{(k)}(\mathbf{r}) = \zeta^{(k)}(\mathbf{r}) - \sum_{l=0}^{k-1} \binom{k}{l} \nabla \cdot (n^{(k-l)}(\mathbf{r}) \nabla \omega^{(l)}(\mathbf{r})). \quad (82)$$

The term $\zeta^{(k)}$ involves multiple commutators of the operators $\hat{q}(\mathbf{r})$ and $\hat{q}'(\mathbf{r})$ with the Hamiltonians \hat{H} and \hat{H}' and their time-derivatives up to order $k-1$, sandwiched between the initial states $|\Psi_0\rangle$ and $|\Phi_0\rangle$. The structure of the iteration procedure is now clear. The inhomogeneity $Q^{(k)}(\mathbf{r})$ is completely determined by the density $n(\mathbf{r}t)$, the potential $v(\mathbf{r}t)$, the initial states $|\Psi_0\rangle$ and $|\Phi_0\rangle$, and the time-derivatives $\partial_t^{(l)} v'(\mathbf{r}t)$ at $t = t_0$ up to order $k-1$. Equation (81) therefore allows for the complete determination of all $\partial_t^k v'(\mathbf{r}t)$ at $t = t_0$. We can therefore construct $v'(\mathbf{r}t)$ from its Taylor series as

$$v'(\mathbf{r}t) = \sum_{k=0}^{\infty} \frac{1}{k!} \partial_t^k v'(\mathbf{r}t) \Big|_{t=t_0} (t - t_0)^k. \quad (83)$$

This determines $v'(\mathbf{r}t)$ completely within the convergence radius of the Taylor expansion. There is, of course, the possibility that the convergence radius is zero. However, this would mean that $v'(\mathbf{r}t)$ and hence $n(\mathbf{r}t)$ and $v(\mathbf{r}t)$ would be non-analytic at $t = t_0$. Since we only consider analytical densities we disregard this possibility. If the convergence radius is nonzero but finite, we can propagate $|\Phi_0\rangle$ to $|\Phi(t_1)\rangle$ at a finite time $t_1 > t_0$ within the convergence radius and repeat the whole procedure above from $t = t_0$ by regarding $|\Phi(t_1)\rangle$ as the initial state. This amounts to analytic continuation along the whole real time-axis and a complete determination of $v'(\mathbf{r}t)$ at all times. We can now make the following statement:

“We specify a given density $n(\mathbf{r}t)$ obtained from a many-particle system with Hamiltonian \hat{H} and initial state $|\Psi_0\rangle$. If one chooses an initial state $|\Phi_0\rangle$ with finite momentum of a many-particle system with two-particle interaction \hat{W}' in such a way that it yields the correct initial density and initial time-derivative of the density, then, for this system, there is a unique external potential $v'(\mathbf{r}t)$ (determined up to a purely time-dependent function $C(t)$) that reproduces the given density $n(\mathbf{r}t)$ ”.

Let us now specify some special cases. We take $\hat{W}' = 0$. We conclude, that for a given initial state $|\Phi_0\rangle$ of finite momentum, with the correct initial density and initial time derivative of the density, there is a unique potential $v_s(\mathbf{r}t)$ (modulo $C(t)$) in a noninteracting system that produces the given density $n(\mathbf{r}t)$ at all times. This solves the noninteracting v -representability problem, provided we can find an initial state with the required properties. If the many-body system described by Hamiltonian

\hat{H} is stationary for times $t < t_0$, the initial state $|\Psi_0\rangle$ at t_0 leads to a density with zero time-derivative at $t = t_0$. In that case a noninteracting state with the required initial density and initial time-derivative of the density (namely zero) can be obtained via the so-called Harriman construction.^{33,34} Therefore a Kohn–Sham potential always exists for this kind of switch-on processes. The additional question whether this initial state can be chosen as a ground state of a noninteracting system is equivalent to the currently unresolved noninteracting- v -representability question for stationary systems.^{25,26}

We now take $\hat{W}' = \hat{W}$. We therefore consider two many-body systems with the same two-particle interaction. For a given v -representable density $n(\mathbf{r}t)$ that corresponds to an initial state $|\Psi_0\rangle$ and potential $v(\mathbf{r}t)$, and for a given initial state $|\Phi_0\rangle$ with the same initial density and initial time derivative of the density, we find that there is a unique external potential $v'(\mathbf{r}t)$ (modulo $C(t)$) that yields this given density $n(\mathbf{r}t)$. The case $|\Psi_0\rangle = |\Phi_0\rangle$ (in which the constraints on the initial state $|\Phi_0\rangle$ are trivially satisfied) corresponds to the well-known Runge–Gross theorem.

2.6. The time-dependent Kohn–Sham approach

In the previous section we found that, under some assumptions, there exists a noninteracting system with the same density as a fully interacting system. We now discuss some properties of this system in more detail. We consider the case that the initial state of the noninteracting system is a single Slater determinant. Usually this will be the ground state Kohn–Sham wavefunction calculated using stationary density-functional theory. The Slater determinant is made up of Kohn–Sham orbitals which satisfy the equations

$$\left[i\partial_t + \frac{1}{2}\nabla^2 - v_s[n](\mathbf{r}t) \right] \varphi_i(\mathbf{r}t) = 0 \quad (84)$$

and the density is constructed as a sum of orbital densities

$$n(\mathbf{r}t) = \sum_{i=1}^N |\varphi_i(\mathbf{r}t)|^2. \quad (85)$$

The Kohn–Sham potential v_s is defined by the requirement that it yields the same density in a noninteracting system. It is defined modulo a purely time-dependent function, i.e. a function that is uniform in space. The choice for v_s can be made unique by requiring that $v_s(\mathbf{r}t) \rightarrow 0$ for $|\mathbf{r}| \rightarrow \infty$. We can subsequently define the exchange-correlation potential by

$$v_s(\mathbf{r}t) = v(\mathbf{r}t) + v_H(\mathbf{r}t) + v_{xc}(\mathbf{r}t), \quad (86)$$

where we defined the Hartree potential as

$$v_H(\mathbf{r}t) = \int d^3r' n(\mathbf{r}'t) w(|\mathbf{r} - \mathbf{r}'|). \quad (87)$$

Note that in this way v_{xc} is not obtained as functional derivative of any functional. In this way we therefore avoid the problems²⁷ related to the definition of an action functional. For practical applications we nevertheless need to find a good approximation for the exchange-correlation potential. For general time-dependent systems this is a difficult problem. However, some information on $v_{xc}(\mathbf{r}t)$ can be obtained from conservation laws. We first consider the momentum $\mathbf{P}_s(t)$ of the Kohn–Sham system, which is identical to the momentum $\mathbf{P}(t)$ of the true system. This follows immediately from

$$\mathbf{P}_s(t) = \int d^3r \mathbf{j}_s(\mathbf{r}t) = \int d^3r r \partial_t n(\mathbf{r}t) = \int d^3r \mathbf{j}(\mathbf{r}t) = \mathbf{P}(t), \quad (88)$$

where we defined the Kohn–Sham current

$$\mathbf{j}_s(\mathbf{r}t) = \frac{1}{2i} \sum_{k=1}^N (\varphi_k^*(\mathbf{r}t) \nabla \varphi_k(\mathbf{r}t) - \varphi_k(\mathbf{r}t) \nabla \varphi_k^*(\mathbf{r}t)). \quad (89)$$

We then obtain immediately, using Eq. (48) that

$$\begin{aligned} 0 = \partial_t(\mathbf{P}(t) - \mathbf{P}_s(t)) &= \int d^3r n(\mathbf{r}t) \nabla (v_s(\mathbf{r}t) - v(\mathbf{r}t)) \\ &= \int d^3r n(\mathbf{r}t) \nabla (v_H(\mathbf{r}t) + v_{xc}(\mathbf{r}t)). \end{aligned} \quad (90)$$

By direct calculation we find that

$$\int d^3r n(\mathbf{r}t) \nabla v_H(\mathbf{r}t) = \int d^3r d^3r' n(\mathbf{r}t) n(\mathbf{r}'t) \frac{\mathbf{r} - \mathbf{r}'}{\rho} \frac{\partial w}{\partial \rho} = 0, \quad (91)$$

where $\rho = |\mathbf{r} - \mathbf{r}'|$, and where we used that the integral is antisymmetric in \mathbf{r} and \mathbf{r}' . We therefore obtain the following equation for the exchange-correlation potential^{11,35}

$$\int d^3r n(\mathbf{r}t) \nabla v_{xc}(\mathbf{r}t) = 0. \quad (92)$$

This equation states that the force exerted on the system by the exchange-correlation potential is zero. From Eq. (88) we also find some condition on the Kohn–Sham current

$$\int d^3r (\mathbf{j}(\mathbf{r}t) - \mathbf{j}_s(\mathbf{r}t)) = \int d^3r \mathbf{j}_{xc}(\mathbf{r}t) = 0, \quad (93)$$

where we defined the exchange-correlation part $\mathbf{j}_{xc}(\mathbf{r}t)$ of the current as the difference of the real and the Kohn–Sham current, i.e. $\mathbf{j}_{xc}(\mathbf{r}t) = \mathbf{j}(\mathbf{r}t) - \mathbf{j}_s(\mathbf{r}t)$. Furthermore, since the density of the Kohn–Sham system is, by definition, equal to the density of the full system, we obtain by subtracting the continuity equations of both systems:

$$0 = \nabla \cdot (\mathbf{j}(\mathbf{r}t) - \mathbf{j}_s(\mathbf{r}t)) = \nabla \cdot \mathbf{j}_{xc}(\mathbf{r}t). \quad (94)$$

We therefore see that $\mathbf{j}_{xc}(\mathbf{r}t)$ is a divergenceless or transversal vector field. A relation between \mathbf{j}_{xc} and v_{xc} is obtained by considering the angular momentum $\mathbf{L}_s(t)$ of the Kohn–Sham system, and the angular momentum $\mathbf{L}(t)$ of the true system. We have

$$\begin{aligned} \int d^3r \mathbf{r} \times \partial_t \mathbf{j}_{xc}(\mathbf{r}t) &= \partial_t (\mathbf{L}(t) - \mathbf{L}_s(t)) \\ &= \int d^3r n(\mathbf{r}) \mathbf{r} \times \nabla (v_s(\mathbf{r}t) - v(\mathbf{r}t)). \end{aligned} \quad (95)$$

By explicit calculation we find that

$$\int d^3r n(\mathbf{r}) \mathbf{r} \times \nabla v_H(\mathbf{r}t) = - \int d^3r d^3r' \mathbf{r} \times \mathbf{r}' n(\mathbf{r}) n(\mathbf{r}') \frac{1}{\rho} \frac{\partial w}{\partial \rho} = 0, \quad (96)$$

where $\rho = |\mathbf{r} - \mathbf{r}'|$ and where we again used the antisymmetry of the integrand.

We thus find

$$\int d^3r \mathbf{r} \times \partial_t \mathbf{j}_{xc}(\mathbf{r}t) = \int d^3r n(\mathbf{r}) \mathbf{r} \times \nabla v_{xc}(\mathbf{r}t). \quad (97)$$

This equation says that the torque due to the exchange-correlation potential is therefore equal to the torque due to the exchange-correlation current. The appearance of an exchange-correlation contribution to the current is a typical feature of a density functional theory based on external scalar fields. There is also a version of density functional theory in which the basic variables are the density and the current.^{36–39} In this theory an additional Kohn–Sham vector potential is introduced to ensure that the Kohn–Sham current is equal to the real current. In that case $\mathbf{j}_{xc} = 0$ and an exchange-correlation vector potential \mathbf{A}_{xc} will appear in the equation for the torque.

3. Linear Response

3.1. Properties of the linear response function

The discussion thusfar was rather general, in the sense that we allowed for arbitrary external potentials and initial states. In this section we will consider a more specific case. A large part of the research in time-dependent systems concerns the calculation of linear response properties. In this case one considers the dynamical reaction of a system that is initially in the ground state, to a small external perturbation. We can then study the linear response of some physical observable to such a small perturbation. In particular we will consider the response of the electron density, as described by the linear density response function. A great deal of information can be obtained from this response function. One can, for instance, obtain the excitation energies of the system since these correspond to poles of this response function in the frequency domain. Let us therefore first investigate some basic properties of this function.

We define the density operator in the Heisenberg picture as

$$\hat{n}_H(\mathbf{r}t) = U(t_0, t) \hat{n}(r) U(t, t_0), \quad (98)$$

where U is the evolution operator corresponding to Hamiltonian \hat{H} . The evolution operator has the property

$$|\Psi(t_2)\rangle = U(t_2, t_1)|\Psi(t_1)\rangle \quad (99)$$

and can formally be defined as

$$U(t_2, t_1) = T \exp \left[-i \int_{t_1}^{t_2} dt \hat{H}(t) \right], \quad (100)$$

where T is the time-ordering operator. In case the Hamiltonian is time-independent U is simply given by $U = \exp(-i\hat{H}(t_2 - t_1))$. If for times $t > t_0$ we perturb the system with a potential $\phi(\mathbf{r}t)$ the linear response of the density is given by

$$\begin{aligned} \delta n(\mathbf{r}_1 t_1) &= -i \int_{t_0}^{t_1} dt_2 d^3 r_2 \langle \Psi_0 | [\hat{n}_H(\mathbf{r}_1 t_1), \hat{n}_H(\mathbf{r}_2 t_2)] | \Psi_0 \rangle \phi(\mathbf{r}_2 t_2) \\ &= \int_{t_0}^{\infty} dt_2 d^3 r_2 \chi_R(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) \phi(\mathbf{r}_2 t_2), \end{aligned} \quad (101)$$

where $|\Psi_0\rangle$ is the ground state wavefunction and where the retarded linear response function χ_R is defined as

$$i\chi_R(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \theta(t_1 - t_2) \langle \Psi_0 | [\hat{n}_H(\mathbf{r}_1 t_1), \hat{n}_H(\mathbf{r}_2 t_2)] | \Psi_0 \rangle. \quad (102)$$

In this equation the subindex H refers to the Hamiltonian of the system before the perturbation $\phi(\mathbf{r}t)$ is switched on. If this initial Hamiltonian is time-independent then χ_R depends on time only through the time interval $t_2 - t_1$. This is the assumption made hereafter. If we insert a complete set of eigenstates of \hat{H} we obtain

$$\chi_R(\mathbf{r}_1, \mathbf{r}_2; t_2 - t_1) = -i\theta(t_2 - t_1) \sum_{\alpha} g_{\alpha}(\mathbf{r}_1) g_{\alpha}^*(\mathbf{r}_2) e^{-i\Omega_{\alpha}(t_2 - t_1)} + \text{c.c.}, \quad (103)$$

where we defined

$$g_{\alpha}(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | N, \alpha \rangle \quad (104)$$

and $\Omega_{\alpha} = E_{\alpha} - E_0$ and where the states $|N, \alpha\rangle$ are N -particle eigenstates of \hat{H} with eigenvalue E_{α} . We see that the energies Ω_{α} are the excitation energies of the system. In the continuous part of the spectrum the sum over index α becomes an integration over α . Since $\phi = 0$ for $t < t_0$ we can extend the time integration in Eq. (101) to $-\infty$ and do the Fourier transform of this equation to obtain

$$\delta \tilde{n}(\mathbf{r}_1 \omega) = \int d^3 r_2 \tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega) \tilde{\phi}(\mathbf{r}_2 \omega), \quad (105)$$

where

$$\tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega) = \int_{-\infty}^{+\infty} d\tau \chi_R(\mathbf{r}_1, \mathbf{r}_2; \tau) e^{i\omega\tau} \quad (106)$$

and \tilde{n} and $\tilde{\phi}$ are defined similarly. The $\tilde{\chi}_R$ is given more explicitly as

$$\tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega) = \lim_{\eta \rightarrow 0^+} \sum_{\alpha} \left\{ \frac{g_{\alpha}(\mathbf{r}_1) g_{\alpha}^*(\mathbf{r}_2)}{\omega - \Omega_{\alpha} + i\eta} - \frac{g_{\alpha}^*(\mathbf{r}_1) g_{\alpha}(\mathbf{r}_2)}{\omega + \Omega_{\alpha} + i\eta} \right\}, \quad (107)$$

where η is a positive infinitesimal whose limit should be taken to be zero from above after integrating the response function with $\tilde{\phi}$. The above form of the response function, known as the Lehmann representation,⁴⁰ clearly displays that poles of the response function correspond to the excitation energies of the system. Because χ_R is a real function, its Fourier transform $\tilde{\chi}_R$ satisfies the symmetry relation

$$\tilde{\chi}_R^*(\mathbf{r}_1, \mathbf{r}_2; \omega) = \tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; -\omega). \quad (108)$$

This means that the real part of $\tilde{\chi}_R$ is an even function of ω and the imaginary part of $\tilde{\chi}_R$ is an odd function of ω . If the system obeys time-reversal symmetry then the eigenstates of \hat{H} can be chosen to be real. In that case the real and imaginary part of $\tilde{\chi}_R$ are given by

$$\text{Re } \tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_{\alpha} g_{\alpha}(\mathbf{r}_1) g_{\alpha}(\mathbf{r}_2) P \left\{ \frac{1}{\omega - \Omega_{\alpha}} - \frac{1}{\omega + \Omega_{\alpha}} \right\} \quad (109)$$

and

$$\text{Im } \tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega) = -\pi \sum_{\alpha} g_{\alpha}(\mathbf{r}_1) g_{\alpha}(\mathbf{r}_2) (\delta(\omega - \Omega_{\alpha}) - \delta(\omega + \Omega_{\alpha})), \quad (110)$$

where P stands for principal value. We indeed see that the real and imaginary part of $\tilde{\chi}_R$ are respectively even and odd functions of the frequency. Since $\tilde{\chi}_R$ is an analytic function in the upper half plane, the real and imaginary parts are related by the Kramers–Kronig relations.² Suppose we look at the discrete part of the spectrum of some finite system. This means that $-I < \omega < I$, where I is the ionization energy of the system. The imaginary part of the response function then consists of a sum of delta functions located at the discrete excitation energies Ω_{α} . This means that if $\omega \neq \Omega_{\alpha}$ then $\tilde{\chi}_R$ is a well-defined real function given by

$$\tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_{\alpha} g_{\alpha}(\mathbf{r}_1) g_{\alpha}(\mathbf{r}_2) \frac{2\Omega_{\alpha}}{\omega^2 - \Omega_{\alpha}^2}. \quad (111)$$

The properties of this function have been investigated by Mearns and Kohn.⁴³ As this function is Hermitian and real, it has a complete orthonormal set of eigenfunctions $\zeta_l(\mathbf{r}, \omega)$ and eigenvalues $\lambda_l(\omega)$:

$$\int d^3r_2 \tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega) \zeta_l(\mathbf{r}_2, \omega) = \lambda_l(\omega) \zeta_l(\mathbf{r}_1, \omega). \quad (112)$$

If the eigenvalue is non-degenerate (apart from the usual additive constant function) then $\lambda_l(\omega) = \lambda_l(-\omega)$ and $\zeta_l(\mathbf{r}, \omega) = \zeta_l(\mathbf{r}, -\omega)$ where ζ_l can be chosen to be real. The response function can then be written in the diagonal form

$$\tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_l \lambda_l(\omega) \zeta_l(\mathbf{r}_1, \omega) \zeta_l(\mathbf{r}_2, \omega), \quad (113)$$

where the eigenvalues $\lambda_l(\omega)$ are given by

$$\lambda_l(\omega) = \sum_{\alpha} \frac{2\Omega_{\alpha}}{\omega^2 - \Omega_{\alpha}^2} |\langle g_{\alpha} | \zeta_l \rangle|^2. \quad (114)$$

Of particular interest to density-functional theory is the question whether $\lambda_l(\omega)$ can be zero for some frequency $\omega = \bar{\omega}$. If this is the case then there are potential changes that yield a zero-density variation. That this is possible has been demonstrated by Mearns and Kohn with the explicit example of noninteracting particles in a box.⁴³ If $\lambda_l(\bar{\omega}) = 0$ for some l (we assume this eigenvalue to be non-degenerate) then, for example, a potential variation δv with Fourier transform,

$$\tilde{v}(\mathbf{r}\omega) = \mu(\delta(\omega - \bar{\omega}) + \delta(\omega + \bar{\omega}))\zeta_l(\mathbf{r}\bar{\omega}), \quad (115)$$

where μ is a arbitrary constant, yields a zero density variation. In the time-domain this corresponds to a potential variation of the form

$$\delta v(\mathbf{r}t) = \frac{\mu}{\pi}\zeta_l(\mathbf{r}\bar{\omega})\cos(\bar{\omega}t). \quad (116)$$

Note, however, that this is an external perturbation that exists at all times, i.e. there is no t_0 such that $\delta v = 0$ for $t < t_0$. In the next section we will prove that for such switch-on potentials zero responses are not possible.

Let us finally discuss the large ω limit and related sum rules for $\tilde{\chi}_R$. From Eq. (107) we see that the large ω limit of χ is given as

$$\tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega) = \frac{c(\mathbf{r}_1, \mathbf{r}_2)}{\omega^2} + O\left(\frac{1}{\omega^4}\right), \quad (\omega \rightarrow \infty), \quad (117)$$

where

$$\begin{aligned} c(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{\alpha} \Omega_{\alpha} (g_{\alpha}(\mathbf{r}_1)g_{\alpha}^*(\mathbf{r}_2) + g_{\alpha}^*(\mathbf{r}_1)g_{\alpha}(\mathbf{r}_2)) \\ &= -\langle \Psi_0 | [[\hat{H}, \hat{n}(\mathbf{r}_1)], \hat{n}(\mathbf{r}_2)] | \Psi_0 \rangle. \end{aligned} \quad (118)$$

The last equality can easily be checked by insertion of a complete set of energy eigenstates. Since $\tilde{\chi}_R$ is analytic in the upper half of the complex ω -plane we find that

$$0 = \int_C d\omega \omega \tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega) = i\pi c(\mathbf{r}_1, \mathbf{r}_2) + \int_{-\infty}^{+\infty} d\omega \omega \tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega), \quad (119)$$

where the contour C is a semi-circle in the upper ω -plane. Since $c(\mathbf{r}_1, \mathbf{r}_2)$ is a real function we obtain

$$\int_{-\infty}^{+\infty} d\omega \omega \operatorname{Im} \tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega) = -\pi c(\mathbf{r}_1, \mathbf{r}_2). \quad (120)$$

For the case of systems with time-reversal symmetry this equation also follows directly by integration of Eq. (110). The obtained result is also known as the f -sum rule in the theory of the electron gas.² In atomic physics the sum rule is often known as the Thomas-Reiche-Kuhn sum rule.¹² If we work out the commutator in Eq. (118) we obtain⁴¹

$$c(\mathbf{r}_1, \mathbf{r}_2) = \nabla_1 \cdot \nabla_2 (\delta(\mathbf{r}_1 - \mathbf{r}_2) n_0(\mathbf{r}_1)), \quad (121)$$

where n_0 is the ground state density. Using the above expression for c , and the asymptotic behavior of $\tilde{\chi}_R$ from Eq. (117), we see that the large ω limit of the induced density response $\delta\tilde{n}$ due to a potential $\delta\tilde{v}$, is given by

$$\delta\tilde{n}(\mathbf{r}\omega) \approx \frac{\nabla \cdot (n_0(\mathbf{r})\nabla\delta\tilde{v}(\mathbf{r}\omega))}{\omega^2}, \quad (\omega \rightarrow \infty). \quad (122)$$

This result is consistent with the previously derived Eq. (54) if one realizes that the behavior of physical quantities for large ω corresponds to their behavior for short times, in our case for $t \approx t_0$. We can invert the above response equation to obtain

$$\delta\tilde{v}(\mathbf{r}_1\omega) \approx \omega^2 \int d^3r_2 a(\mathbf{r}_1, \mathbf{r}_2) \delta\tilde{n}(\mathbf{r}_2\omega), \quad (\omega \rightarrow \infty), \quad (123)$$

where a satisfies

$$\nabla_1 \cdot (n_0(\mathbf{r}_1)\nabla_1 a(\mathbf{r}_1, \mathbf{r}_2)) = \delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (124)$$

The function a is therefore the Green function corresponding to the Sturm–Liouville equation discussed before. If we require that a vanishes at infinity then there is a unique solution for this function. One can then further show, using Green’s theorem,⁴² that a is symmetric, i.e. $a(\mathbf{r}_1, \mathbf{r}_2) = a(\mathbf{r}_2, \mathbf{r}_1)$. This implies the following relation for the inverse response function

$$\tilde{\chi}_R^{-1}(\mathbf{r}_1, \mathbf{r}_2; \omega) \approx \omega^2 a(\mathbf{r}_1, \mathbf{r}_2), \quad (\omega \rightarrow \infty). \quad (125)$$

One can therefore conclude that, for short times, the inverse density response function in the time domain behaves like the second derivative of the delta function. This is, of course, reflected in the second time-derivative of the density in Eq. (54). The general form of $\tilde{\chi}_R^{-1}$ for large frequencies is given by

$$\tilde{\chi}_R^{-1}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \omega^2 a(\mathbf{r}_1, \mathbf{r}_2) + b(\mathbf{r}_1, \mathbf{r}_2) + O\left(\frac{1}{\omega^2}\right), \quad (\omega \rightarrow \infty), \quad (126)$$

where the function b is determined from the ω^{-4} -coefficient in the large ω -expansion of $\tilde{\chi}_R$. This coefficient in turn is determined from the so-called third frequency moment sum rule⁴¹ and will not be discussed here. This general form implies in the time-domain that

$$\begin{aligned} \chi_R^{-1}(\mathbf{r}_1, \mathbf{r}_2; t_2 - t_1) &= \delta''(t_2 - t_1) a(\mathbf{r}_1, \mathbf{r}_2) + \delta(t_2 - t_1) b(\mathbf{r}_1, \mathbf{r}_2) \\ &\quad + h_{\text{reg}}(\mathbf{r}_1, \mathbf{r}_2; t_2 - t_1). \end{aligned} \quad (127)$$

Here δ'' is the second derivative of the delta function and where h_{reg} is the regular part of χ^{-1} , where the use of the word regular refers to the absence of delta functions in the time variable. The regular part h_{reg} is a causal function, i.e. $h_{\text{reg}} = 0$ for $t_1 > t_2$. The inverse response function has the same causal structure as the original response function. This can be seen directly from a discretization of the time variable because the inverse of an upper triangular matrix is again an upper triangular matrix.

Thusfar we have been discussing the properties of the response function and its inverse without a discussion of the conditions under which an inverse can be obtained. This will be the topic of the next section.

3.2. *An invertability proof for switch-on processes*

In this section we will address the question if we can recover the potential variation $\delta v(\mathbf{r}t)$ from a given density variation $\delta n(\mathbf{r}t)$ that was produced by it. There is, of course, an obvious non-uniqueness since both $\delta v(\mathbf{r}t)$ and $\delta v(\mathbf{r}t) + C(t)$, where $C(t)$ is an arbitrary time-dependent function, produce the same density variation. However, this is simply a gauge of the potential and is easily taken care of. Thus by an inverse we will always mean an inverse modulo a purely time-dependent function $C(t)$ and by different potentials we will always mean that they differ more than a gauge $C(t)$.

From the work of Mearns and Kohn⁴³ we know that different potentials can yield the same density variations. However, in their examples these potentials are always potentials that exist at all times, i.e. there is no t_0 such that $\delta v = 0$ for times $t < t_0$. On the other hand we know from the Runge–Gross proof that a potential $\delta v(\mathbf{r}t)$ (not purely time-dependent) that is switched on at $t = t_0$ and is analytic in t_0 always causes a nonzero density variation $\delta n(\mathbf{r}t)$. In this proof the first nonvanishing time-derivative of δn at t_0 is found to be linear in the corresponding derivative of δv and therefore the linear response function is invertible. Note that this conclusion is even true for an arbitrary initial state. The conclusion is therefore true for linear response to an already time-dependent system for which the linear response function will depend on both t and t' separately, rather than on the time-difference $t - t'$. In the following we will give an explicit proof for the invertability of the linear response function for which the system is initially in its ground state. However we will relax the condition that δv be an analytic function in time, and we therefore allow for a larger class of external potentials than assumed in the Runge–Gross theorem.

We consider a many-body system in its ground state. At $t = 0$ (since the system is initially described by a time-independent Hamiltonian we can, without loss of generality, put the initial time $t_0 = 0$) we switch on an external field $\phi(\mathbf{r}t)$ which causes a density response δn . We want to show that the linear response function is invertable for these switch-on processes. The density response is given by

$$\delta n(\mathbf{r}_1 t_1) = -i \int_0^{t_1} dt_2 d^3 r_2 \langle \Psi_0 | [\Delta \hat{n}_H(\mathbf{r}_1 t_1), \Delta \hat{n}_H(\mathbf{r}_2 t_2)] | \Psi_0 \rangle \phi(\mathbf{r}_2 t_2). \quad (128)$$

Note that here, instead of the density operator \hat{n}_H , we prefer to use the density fluctuation operator $\Delta \hat{n}_H = \hat{n}_H - \langle \hat{n}_H \rangle$ in the response function. This is not in conflict with Eq. (101) since the commutator of the density operators is equal to the commutator of the density fluctuation operators. Now we insert a complete set

of eigenstates of \hat{H} and we find

$$\begin{aligned}\delta n(\mathbf{r}_1 t_1) &= i \sum_n \int_0^{t_1} dt_2 d^3 r_2 \langle \Psi_0 | \Delta \hat{n}_H(\mathbf{r}_2 t_2) | \Psi_n \rangle \\ &\quad \times \langle \Psi_n | \Delta \hat{n}_H(\mathbf{r}_1 t_1) | \Psi_0 \rangle \phi(\mathbf{r}_2 t_2) + \text{c.c.} \\ &= i \sum_n \int_0^{t_1} dt_2 d^3 r_2 e^{i\Omega_n(t_1-t_2)} f_n^*(\mathbf{r}_1) f_n(\mathbf{r}_2) \phi(\mathbf{r}_2 t_2) + \text{c.c.}\end{aligned}\quad (129)$$

where $\Omega_n = E_n - E_0 > 0$ are the excitation energies of the unperturbed system (we assume the ground state to be nondegenerate) and the functions f_n are defined as

$$f_n(\mathbf{r}) = \langle \Psi_0 | \Delta \hat{n}(\mathbf{r}) | \Psi_n \rangle. \quad (130)$$

This response can also be written as

$$\delta n(\mathbf{r}_1 t_1) = i \sum_n f_n^*(\mathbf{r}_1) \int_0^{t_1} dt_2 a_n(t_2) \exp[i\Omega_n(t_1 - t_2)] + \text{c.c.} \quad (131)$$

where we defined

$$a_n(t) = \int d^3 r f_n(\mathbf{r}) \phi(\mathbf{r}t). \quad (132)$$

Now we note the time integral in Eq. (131) is exactly of a convolution form. This means that we can simplify this equation using Laplace transforms. The Laplace transform is defined by

$$Lf(s) = \int_0^\infty dt e^{-st} f(t) \quad (133)$$

and we want to use its basic convolution property

$$L(f * g)(s) = Lf(s)Lg(s), \quad (134)$$

where the convolution product is defined as

$$(f * g)(t) = \int_0^t d\tau f(\tau)g(t - \tau). \quad (135)$$

If we now take the Laplace transform of δn we obtain the equation:

$$L(\delta n)(\mathbf{r}_1 s) = i \sum_n f_n^*(\mathbf{r}_1) \frac{1}{s - i\Omega_n} La_n(s) + \text{c.c.} \quad (136)$$

If we multiply both sides with the Laplace transform $L\phi$ of ϕ and integrate over \mathbf{r}_1 we obtain

$$\int d^3 r_1 L\phi(\mathbf{r}_1 s) L(\delta n)(\mathbf{r}_1 s) = i \sum_n \frac{1}{s - i\Omega_n} |La_n(s)|^2 + \text{c.c.} \quad (137)$$

We therefore obtain

$$\int d^3 r_1 L\phi(\mathbf{r}_1 s) L(\delta n)(\mathbf{r}_1 s) = -2 \sum_n \frac{\Omega_n}{s^2 + \Omega_n^2} |La_n(s)|^2. \quad (138)$$

This is the basic relation that we use to prove invertability. If we assume that $\delta n = 0$ then also $L(\delta n) = 0$ and we obtain

$$0 = \sum_n \frac{\Omega_n}{s^2 + \Omega_n^2} |La_n(s)|^2. \quad (139)$$

However since each prefactor of $|La_n|^2$ in the summation is positive the sum can only be zero if $La_n = 0$ for all n . This in its turn implies that $a_n(t)$ must be zero for all n . This means also that

$$\begin{aligned} \int d^3r \Delta \hat{n}(r) \phi(\mathbf{r}t) |\Psi_0\rangle &= \sum_n |\Psi_n\rangle \int d^3r \langle \Psi_n | \Delta \hat{n}(\mathbf{r}) | \Psi_0 \rangle \phi(\mathbf{r}t) \\ &= \sum_n a_n(t) |\Psi_n\rangle = 0. \end{aligned} \quad (140)$$

Note that $a_0(t)$ is automatically zero since obviously $\langle \Psi_0 | \Delta \hat{n}(x) | \Psi_0 \rangle = 0$. If we write out the above equation in first quantization again we have

$$\sum_{k=1}^N \Delta \phi(\mathbf{r}_k t) |\Psi_0\rangle = 0, \quad (141)$$

where N is the number of electrons in the system and $\Delta \phi(\mathbf{r}t)$ is defined as

$$\Delta \phi(\mathbf{r}t) = \phi(\mathbf{r}t) - \frac{1}{N} \int d^3r n_0(\mathbf{r}) \phi(\mathbf{r}t), \quad (142)$$

where n_0 is the density of the unperturbed system. Now Eq. (141) immediately implies that $\Delta \phi = 0$ and, since the second term on the right hand side of Eq. (142) is a purely time-dependent function, we obtain

$$\phi(\mathbf{r}t) = C(t). \quad (143)$$

We have therefore proven that only purely time-dependent potentials yield zero density response. In other words the response function is invertible for switch-on processes. Note that the only restriction we put on the potential $\phi(\mathbf{r}t)$ is that it is Laplace-transformable. This is a much weaker restriction on the potential than the constraint that it be an analytic function in $t = t_0$, as required in the Runge–Gross proof.

Another consequence of the above analysis is the following. Suppose the linear response kernel has eigenfunctions, i.e. there is a λ such that

$$\lambda \zeta(r_1 t_1) = \int dt_2 d^3r_2 \chi_R(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) \zeta(\mathbf{r}_2 t_2). \quad (144)$$

Laplace transforming this equation yields

$$\lambda L\zeta(\mathbf{r}_1 s) = \int d^3r_2 \Xi(\mathbf{r}_1, \mathbf{r}_2; s) L\zeta(\mathbf{r}_2 s), \quad (145)$$

where Ξ is the Laplace transform of χ explicitly given by

$$\Xi(\mathbf{r}_1, \mathbf{r}_2; s) = i \sum_n \frac{f_n^*(\mathbf{r}_1) f_n(\mathbf{r}_2)}{s - i\Omega_n} + \text{c.c.} \quad (146)$$

Since Ξ is a real Hermitian operator its eigenvalues λ are real and its eigenfunctions $L\zeta$ can be chosen to be real. Then ζ is real as well and Eq. (138) implies (if we take $\phi = \zeta$ and $\delta n = \lambda\zeta$)

$$\lambda \int d^3r (L\zeta(\mathbf{r}\mathbf{s}))^2 < 0, \quad (147)$$

which implies $\lambda < 0$. We have therefore proven that if there are density variations that are proportional to the applied potential, then this constant of proportionality is negative. In other words, the eigenvalues of the density response function are negative. In this derivation we made again explicit use of Laplace transforms and therefore of the condition that $\zeta = 0$ for $t < 0$. The work of Mearns and Kohn shows that positive eigenvalues are possible when this restriction is not made.

3.3. The exchange-correlation kernel and linear response in TDDFT

Now that we have learned about some properties of the density response function we will discuss how we can calculate this function within density functional theory. The determination of this function is of great practical use, since it contains all the information on the excitation energies. In TDDFT one calculates this function by solving an equation that relates the exact density response function to the density response function of the Kohn–Sham system. In order to derive this equation we first define the exchange-correlation kernel f_{xc} as:

$$f_{xc}(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta v_{xc}(\mathbf{r}t)}{\delta n(\mathbf{r}'t')}. \quad (148)$$

This kernel describes the change in the exchange-correlation potential $v_{xc}(\mathbf{r}t)$ due to density variations $\delta n(\mathbf{r}'t')$. Once we can find a good approximation for this function we are able to calculate the density response function. This is seen as follows. We calculate, using the chain rule for differentiation

$$\frac{\delta n(\mathbf{r}_1 t_1)}{\delta v(\mathbf{r}_2 t_2)} = \int dt_3 d^3r_3 \frac{\delta n(\mathbf{r}_1 t_1)}{\delta v_s(\mathbf{r}_3 t_3)} \frac{\delta v_s(\mathbf{r}_3 t_3)}{\delta v(\mathbf{r}_2 t_2)}. \quad (149)$$

The function on the left hand side of this equation is simply the density response function χ_R . The first term under the integral sign on the right hand side is the density response function of the Kohn–Sham system, which we will denote as $\chi_{R,s}$. It gives the change in the density as a result of a change in the Kohn–Sham potential. The second term under the integral sign gives the change in the Kohn–Sham potential due to a change in the external field. We can work out this term as:

$$\begin{aligned} \frac{\delta v_s(\mathbf{r}_3 t_3)}{\delta v(\mathbf{r}_2 t_2)} &= \delta(\mathbf{r}_3 - \mathbf{r}_2) \delta(t_3 - t_2) + \int dt_4 d^3r_4 [w(|\mathbf{r}_3 - \mathbf{r}_4|) \delta(t_3 - t_4) \\ &\quad + f_{xc}(\mathbf{r}_3 t_3, \mathbf{r}_4 t_4)] \frac{\delta n(\mathbf{r}_4 t_4)}{\delta v(\mathbf{r}_2 t_2)}. \end{aligned} \quad (150)$$

If we now collect our results we obtain the basic relation:

$$\begin{aligned}\chi_R(1, 2) = \chi_{R,s}(1, 2) + \int d3d4 \chi_{R,s}(1, 3)(w(|\mathbf{r}_3 - \mathbf{r}_4|)\delta(t_3 - t_4) \\ + f_{xc}(3, 4))\chi_R(4, 2),\end{aligned}\quad (151)$$

where we introduced the short notation $i = \mathbf{r}_i t_i$ and $di = d^3 r_i dt_i$. This relation relates the response function of the Kohn–Sham system to the response function of the interacting system. In order to solve this equation we need to find, as always, a good approximation for the exchange-correlation kernel f_{xc} . Equation (151) has by now found many applications and many properties of molecules^{46,47} and solids¹² that have been obtained this way were in good agreement with experiment. These calculations are almost always carried out with the simple adiabatic local density approximation for f_{xc} .¹² This approximation is surprisingly succesful. Nevertheless there are deficiencies and therefore we will investigate some exact properties of f_{xc} which will be of some help to judge approximate functionals.

From the fact that χ_R and $\chi_{R,s}$ only depend on the differences of their time arguments we find from this equation that also f_{xc} has this property. We can therefore define the Fourier transform of f_{xc} by

$$\tilde{f}_{xc}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \int_{-\infty}^{+\infty} d\tau f_{xc}(\mathbf{r}_1, \mathbf{r}_2; \tau) e^{i\omega\tau} \quad (152)$$

where $\tau = t_2 - t_1$. In the frequency domain the integral equation for χ_R therefore becomes

$$\begin{aligned}\tilde{\chi}_R(\mathbf{r}_1, \mathbf{r}_2; \omega) = \tilde{\chi}_{R,s}(\mathbf{r}_1, \mathbf{r}_2; \omega) + \int d\mathbf{r}_3 d\mathbf{r}_4 \tilde{\chi}_{R,s}(\mathbf{r}_1, \mathbf{r}_3; \omega)(w(|\mathbf{r}_3 - \mathbf{r}_4|) \\ + \tilde{f}_{xc}(\mathbf{r}_3, \mathbf{r}_4; \omega))\tilde{\chi}_R(\mathbf{r}_4, \mathbf{r}_2; \omega).\end{aligned}\quad (153)$$

Within this expression the Kohn–Sham response function can be given explicitly in terms of the Kohn–Sham orbitals

$$\tilde{\chi}_{R,s}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \lim_{\eta \rightarrow 0+} \sum_{kl} (\mu_l - \mu_k) \frac{\varphi_k(\mathbf{r}_1)\varphi_l^*(\mathbf{r}_1)\varphi_k^*(\mathbf{r}_2)\varphi_l(\mathbf{r}_2)}{\omega - (\epsilon_k - \epsilon_l) + i\eta}, \quad (154)$$

where μ_k is ground state occupation number of orbital ϕ_k , i.e. $\mu_k = 1$ for occupied states and $\mu_k = 0$ for unoccupied states. As we see the Kohn–Sham response function has poles at differences in the Kohn–Sham orbital energies. The role of the exchange-correlation kernel f_{xc} is to shift these energy differencies to the true excitation energies. For this kernel we find the following formal expression:

$$\tilde{f}_{xc}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \tilde{\chi}_{R,s}^{-1}(\mathbf{r}_1, \mathbf{r}_2; \omega) - \tilde{\chi}_R^{-1}(\mathbf{r}_1, \mathbf{r}_2; \omega) - w(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (155)$$

Since both $\tilde{\chi}_R^{-1}$ and $\tilde{\chi}_{R,s}^{-1}$ are causal functions also \tilde{f}_{xc} is a causal function and is analytical in the upper half ω -plane. We can further derive some properties of f_{xc}

in the high frequency limit. The high frequency limits of the exact and Kohn–Sham response functions are given by (see Eq. (126):

$$\tilde{\chi}_R^{-1}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \omega^2 a(\mathbf{r}_1, \mathbf{r}_2) + b(\mathbf{r}_1, \mathbf{r}_2) + O\left(\frac{1}{\omega^2}\right), \quad (\omega \rightarrow \infty) \quad (156)$$

$$\tilde{\chi}_{R,s}^{-1}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \omega^2 a(\mathbf{r}_1, \mathbf{r}_2) + b_s(\mathbf{r}_1, \mathbf{r}_2) + O\left(\frac{1}{\omega^2}\right), \quad (\omega \rightarrow \infty). \quad (157)$$

The leading term proportional to ω^2 is equal for χ_R^{-1} and $\chi_{R,s}^{-1}$ in both equations. This is because $a(\mathbf{r}_1, \mathbf{r}_2)$ is completely determined by the ground state density n_0 (see Eq. (124)) which by definition is equal for the Kohn–Sham system and the real system. We therefore obtain for the large frequency limit of f_{xc}

$$f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega) = b_s(\mathbf{r}_1, \mathbf{r}_2) - b(\mathbf{r}_1, \mathbf{r}_2) - w(|\mathbf{r}_1 - \mathbf{r}_2|) + O\left(\frac{1}{\omega^2}\right), \quad (\omega \rightarrow \infty). \quad (158)$$

The exchange-correlation kernel f_{xc} therefore approaches a finite value in the high-frequency limit. The form of the functions b and b_s can be determined from the third frequency moment sum rule.⁴¹

Let us further investigate the behavior of f_{xc} in the low-frequency regime. We consider the discrete part of the spectrum of a finite system. Therefore the frequency range is given by $-I < \omega < I$, where I is the ionization energy. In this frequency range the inverse response function is given as

$$\tilde{\chi}_R^{-1}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_l \frac{1}{\lambda_l(\omega)} \zeta_l(\mathbf{r}_1, \omega) \zeta_l(\mathbf{r}_2, \omega), \quad (159)$$

where $\zeta_l(\mathbf{r}\omega)$ and $\lambda_l(\omega)$ are the eigenfunctions and eigenvalues of the response function $\tilde{\chi}_R$. The inverse density response of the Kohn–Sham system can be written in a similar way:

$$\tilde{\chi}_{R,s}^{-1}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_l \frac{1}{\lambda_{l,s}(\omega)} \zeta_{l,s}(\mathbf{r}_1, \omega) \zeta_{l,s}(\mathbf{r}_2, \omega), \quad (160)$$

where $\zeta_{l,s}(\mathbf{r}\omega)$ and $\lambda_{l,s}(\omega)$ are the eigenfunctions and eigenvalues of the response function $\tilde{\chi}_{R,s}$. It is important to note that the frequency range in which the Kohn–Sham system has a discrete spectrum coincides with the frequency range in which the real system has its discrete spectrum. This is because both systems have identical ionization energies, i.e. the eigenvalue of the highest occupied Kohn–Sham orbital is equal in absolute value to the ionisation energy. From Eq. (155) we then see that f_{xc} has a discrete spectrum for $-I < \omega < I$ and is given by

$$\begin{aligned} f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega) &= \sum_l \frac{1}{\lambda_{l,s}(\omega)} \zeta_{l,s}(\mathbf{r}_1, \omega) \zeta_{l,s}(\mathbf{r}_2, \omega) \\ &\quad - \sum_l \frac{1}{\lambda_l(\omega)} \zeta_l(\mathbf{r}_1, \omega) \zeta_l(\mathbf{r}_2, \omega) - w(|\mathbf{r}_1 - \mathbf{r}_2|). \end{aligned} \quad (161)$$

We therefore see that f_{xc} has a pole in the discrete spectrum whenever $\lambda_l(\omega) = 0$ or $\lambda_{l,s}(\omega) = 0$. In actual calculations we are interested in f_{xc} near an excitation energy where f_{xc} has no poles. However, since a pole of f_{xc} is always in between two excitation energies the pole structure of f_{xc} can become important when two excitation energies approach each other. This could happen, for instance, in molecular dissociation situations where bonding and anti-bonding states become nearly degenerate and where the pole of f_{xc} is squeezed between these nearly degenerate energies which leads to a divergence of the exchange-correlation kernel.

Thusfar we have investigated the frequency-dependence of the exchange-correlation kernel. One could imagine also some situations in which the spatial dependence of f_{xc} plays an important role. One case where this is the case is in the metal-insulator transition. At the transition point the analytic behavior of the density response function changes abruptly. This is because in the insulating phase, a test charge is only partially screened at large distances whereas the screening is complete in the metallic case. This screening is directly related to the long-range spatial properties of the density response function. Now the metal-insulator transition does not occur at the same time for the Kohn-Sham system, since the gap in the Kohn-Sham eigenvalue spectrum does, in general, not coincide with the real gap. This question has been investigated numerically by Godby and Needs.⁴⁴ In this work they found that, when one compresses an insulating system, the exact density functional gap closes long before the real system becomes metallic. This implies that the exchange-correlation kernel f_{xc} must have two changes of analytic behavior if an insulating material is compressed. There is one change when the Kohn-Sham system becomes metallic and another one when the real system becomes metallic. This is the price one has to pay for converting the many-body problem into an equivalent one-particle theory.

4. The Action Functional

4.1. *v-representability and boundary conditions*

One of the main problems of obtaining good approximate solutions to the time-dependent Schrödinger equation is to find a criterium for the accuracy of approximate wavefunctions. In the ground state case there is the Raleigh-Ritz variational principle which says that the normalized wavefunction which minimizes the expectation value of the Hamiltonian is equal to the wavefunction of the ground state. The energy expectation value can therefore be used as a criterium to judge the accuracy of the method. Several methods such as Configuration Interaction (CI) and Quantum Monte Carlo (QMC)⁴⁵ are based on this criterium. However, such a simple criterium does not exist for the time-dependent case. One of the first things one might think of is to consider the error function

$$|\Theta(t)\rangle = (i\partial_t - \hat{H}(t))|\Phi(t)\rangle \quad (162)$$

and try to minimize the norm $\langle \Theta | \Theta \rangle$ of this error function over a set of normalized Φ 's. Such a procedure is described by Löwdin and Mukherjee.⁴⁸ However, the corresponding variational equations are quadratic in the Hamiltonian and therefore difficult to solve. For practical applications we should seek simpler procedures.

Much work on time-dependent systems has been based on Frenkel's variational principle

$$\langle \delta \Psi | i\partial_t - \hat{H}(t) | \Psi \rangle = 0. \quad (163)$$

In practical applications of this principle Ψ usually corresponds to some parametrized Ansatz of the wavefunction and $\delta \Psi$ is obtained by making variations with respect to these parameters.⁴⁹ This amounts to doing a restricted set of variations. If we are allowed to make completely arbitrary variations of the wavefunction Frenkel's variational principle is equivalent to the time-dependent Schrödinger equation. This is easily seen by taking

$$|\delta \Psi\rangle = \epsilon(i\partial_t - \hat{H}(t))|\Psi\rangle, \quad (164)$$

where ϵ is a small parameter. In that case Frenkel's variational principle tells us that $\langle \delta \Psi | \delta \Psi \rangle = 0$ and therefore

$$|\delta \Psi\rangle = \epsilon(i\partial_t - \hat{H}(t))|\Psi\rangle = 0 \quad (165)$$

which is the time-dependent Schrödinger equation. It is clear that Frenkel's variational principle is quite different from the usual variational principle for the ground state since no quantity is optimized. This makes it also difficult to define a density functional on the basis of this variational principle. There is, however, a well-known principle based on the following time-dependent action functional

$$A[\Psi] = \int_{t_0}^{t_1} dt \langle \Psi | i\partial_t - \hat{H}(t) | \Psi \rangle. \quad (166)$$

The usual approach is to require the action to be stationary under variations $\delta \Psi$ which satisfy $\delta \Psi(t_0) = \delta \Psi(t_1) = 0$. We then find after a partial integration

$$\delta A = \int_{t_0}^{t_1} dt \langle \delta \Psi | i\partial_t - \hat{H}(t) | \Psi \rangle + \text{c.c.} + [i \langle \Psi | \delta \Psi \rangle]_{t_0}^{t_1}. \quad (167)$$

With the boundary conditions on the variations $\delta \Psi$ the last term disappears and we have the stationarity condition

$$0 = \delta A = 2 \operatorname{Re} \int_{t_0}^{t_1} dt \langle \delta \Psi | i\partial_t - \hat{H}(t) | \Psi \rangle. \quad (168)$$

If we split the variation $\delta \Psi = \delta \Psi_1 + i\delta \Psi_2$ where $\delta \Psi_1$ and $\delta \Psi_2$ are real functions, we obtain (using $\operatorname{Re}(iz) = -\operatorname{Im}(z)$) that

$$0 = \delta A = 2 \operatorname{Re} \int_{t_0}^{t_1} dt \langle \delta \Psi_1 | i\partial_t - \hat{H}(t) | \Psi \rangle - 2 \operatorname{Im} \int_{t_0}^{t_1} dt \langle \delta \Psi_2 | i\partial_t - \hat{H}(t) | \Psi \rangle. \quad (169)$$

Since $\delta\Psi_1$ and $\delta\Psi_2$ can be varied independently we obtain the result that the real and imaginary parts of $(i\partial_t - \hat{H}(t))|\Psi\rangle$ are equal to zero. In other words

$$(i\partial_t - \hat{H}(t))|\Psi\rangle = 0, \quad (170)$$

which is just the time-dependent Schrödinger equation. We see that the variational requirement $\delta A = 0$, together with the boundary conditions is equivalent to the time-dependent Schrödinger equation.

A different derivation⁴⁸ which does not put any constraints on the variations at the endpoints of the time interval is the following. We consider again a first order change in the action due to changes in the wavefunction and require that the action is stationary. We have the general relation

$$0 = \delta A = \int_{t_0}^{t_1} dt \langle \delta\Psi | i\partial_t - \hat{H}(t) | \Psi \rangle + \int_{t_0}^{t_1} dt \langle \Psi | i\partial_t - \hat{H}(t) | \delta\Psi \rangle. \quad (171)$$

We now choose the variations $\delta\Psi = \delta\Phi$ and $\delta\Psi = i\delta\Phi$ where $\delta\Phi$ is arbitrary. We thus obtain

$$0 = \delta A = \int_{t_0}^{t_1} dt \langle \delta\Phi | i\partial_t - \hat{H}(t) | \Psi \rangle + \int_{t_0}^{t_1} dt \langle \Psi | i\partial_t - \hat{H}(t) | \delta\Phi \rangle \quad (172)$$

and

$$0 = \delta A = -i \int_{t_0}^{t_1} dt \langle \delta\Phi | i\partial_t - \hat{H}(t) | \Psi \rangle + i \int_{t_0}^{t_1} dt \langle \Psi | i\partial_t - \hat{H}(t) | \delta\Phi \rangle. \quad (173)$$

From the two above equations we obtain

$$0 = \int_{t_0}^{t_1} dt \langle \delta\Phi | i\partial_t - \hat{H}(t) | \Psi \rangle. \quad (174)$$

Since this must be true for arbitrary $\delta\Phi$ we again obtain the time-dependent Schrödinger equation

$$(i\partial_t - \hat{H}(t))|\Psi\rangle = 0. \quad (175)$$

We did not need to put any boundary conditions on the variations at all. We only required that if $\delta\Phi$ is an allowed variation that then also $i\delta\Phi$ is an allowed variation.

With the two derivations above we thus have shown that we can derive the time-dependent Schrödinger equation from an action principle based on the action functional (166). The numerical value of action functional itself can however not be used as a criterium to judge the accuracy of a given Ansatz for the wavefunction. If we allow for complete variational freedom in the variations of the wavefunction, our solution will satisfy the time-dependent Schrödinger equation exactly and the action will be identical zero. Usually our variational freedom will be restricted, as we will restrict our trial wavefunctions, for instance using orbital products, or time-dependent parameters that fix the shape of our trial wavefunction. In that case the value of the action at the solution point of the variational equations need not be zero. Nevertheless a wavefunction Φ , with zero value of the action $A[\Phi] = 0$, can

always be obtained from an approximate variational solution Ψ by defining a new wavefunction

$$|\Phi\rangle = \exp\left(-i \int_{t_0}^t dt \frac{\langle\Psi|i\partial_t - \hat{H}(t)|\Psi\rangle}{\langle\Psi|\Psi\rangle}\right)|\Psi\rangle. \quad (176)$$

This corresponds to multiplication of the solution by a purely time-dependent factor. There are therefore always approximate wavefunctions that yield an action that is identically zero and this value can therefore not be used to judge the accuracy of a given approximation. In general $A = 0$ at the solution point of the variational equations for any parametrization of the wavefunction that allows for a variation of the form $\delta\Phi = C(t)\Psi$ where $C(t)$ is an arbitrary function of time. This follows immediately by inserting this variation into Eq. (174). In that case one obtains

$$0 = \langle\Psi|i\partial_t - \hat{H}(t)|\Psi\rangle. \quad (177)$$

Such a variation is, for instance, allowed in an approximate wavefunction that is a product of orbitals by making an orbital variation $\delta\phi_i(\mathbf{r}t) = C(t)\phi_i(\mathbf{r}t)$. For this reason the variational solution of the time-dependent Hartree–Fock equations corresponds to a zero value of the action integrand. Since in general

$$\partial_t \langle\Phi|\Phi\rangle = 2 \operatorname{Im} \langle\Phi|i\partial_t - \hat{H}(t)|\Phi\rangle, \quad (178)$$

it follows that if Eq. (177) is satisfied then also the norm of $|\Phi\rangle$ is conserved. From our discussion above we can immediately conclude that the time-dependent Hartree–Fock equations conserve the norm of the wavefunction.

Let us now discuss the problems with the variational principle when one attempts to construct a time-dependent density-functional theory. The obvious definition of a density functional would be

$$A[n] = \int_{t_0}^{t_1} dt \langle\Psi[n]|i\partial_t - \hat{H}(t)|\Psi[n]\rangle, \quad (179)$$

where $|\Psi[n]\rangle$ is a wavefunction which yields density $n(\mathbf{r}t)$ and evolves from a given initial state $|\Psi_0\rangle$ with initial density $n_0(\mathbf{r})$. By the Runge–Gross theorem such a wavefunction is determined up to a phase factor. In order to define the action uniquely we have to make a choice for this phase factor. We could for instance choose a phase factor for each $|\Psi\rangle$ such that $\langle\Psi|i\partial_t - \hat{H}(t)|\Psi\rangle = 0$. This is a choice made in Eq. (176). However, as is obvious this leads to a rather useless functional which is identically zero. Another choice would be to choose the $|\Psi[n]\rangle$ that evolves in the external potential $v(\mathbf{r}t)$ that vanishes at infinity and yields density $n(\mathbf{r}t)$. This corresponds to a choosing a particular kind of gauge. There are of course many more phase conventions possible. The trouble obviously arises from the fact that the density only determines the wavefunction up to an arbitrary time-dependent phase. However, there are more problems. Suppose we avoid the phase problem by defining a functional of the external potential rather than the density

$$A[v] = \int_{t_0}^{t_1} dt \langle\Psi[v]|i\partial_t - \hat{H}(t)|\Psi[v]\rangle. \quad (180)$$

Note that the potential v in the argument of the action is only used to parametrize the set of wavefunctions used in the action principle. This potential v is therefore not the same as the external potential in the Hamiltonian $\hat{H}(t)$ as this Hamiltonian is fixed. The state $|\Psi[v]\rangle$ is a state that evolves from a given initial state $|\Psi_0\rangle$ by solution of a time-dependent Schrödinger equation with potential v as its external potential. As the potential obviously defines $|\Psi[v]\rangle$ uniquely, including its phase, the action is well-defined. The action is not a density functional but since the functional is now well-defined, one could now try to construct a density functional from it afterwards, for instance using a Legendre transform. However, even this strategy is not successful. Requiring $\delta A = 0$ for variations δv in the potential still does not yield the Schrödinger equation. The reason for this is that all variations $\delta\Psi$ of the wavefunction must now be caused by potential variations δv which leads to variations over a restricted set of wavefunctions. In other words, the variations $\delta\Psi$ must be v -representable. For instance, when deriving the Schrödinger equation from the variational principle one can not assume the boundary conditions $\delta\Psi(t_0) = \delta\Psi(t_1) = 0$. Since the time-dependent Schrödinger equation is first order in time, the variation $\delta\Psi(t)$ at times $t > t_0$ is completely determined by the boundary condition for $\delta\Psi(t_0)$. We are thus no longer free to specify a second boundary condition at a later time t_1 . Moreover, we are not allowed to treat the real and imaginary part of $\delta\Psi$ as independent variations since both are determined by the potential variation δv . This means that the first derivation of the TDSE that we presented in this section, can not be carried out. It is readily seen that also the second derivation based on Eqs. (172) and (173) fails. If $\delta\Psi$ is a variation generated by some δv , then $\delta\Psi$ satisfies

$$(i\partial_t - \hat{H}_v(t))|\delta\Psi\rangle = \delta v|\Psi\rangle, \quad (181)$$

where \hat{H}_v is a Hamiltonian with potential v and we neglected terms of higher order. Multiplication by the imaginary number i yields that variation $i\delta\Psi$ must be generated by potential $i\delta v$. This potential variation is however imaginary and therefore not an allowed variation since all potential variations must be real.

We therefore conclude that time-dependent density-functional theory can not be based on the usual variational principle, and indeed attempts to do so have led to paradoxes. In the next section we will show how an extended type of action functional defined on a time-contour can be used as a basis from which the time-dependent Kohn–Sham equations can be derived.

4.2. *The Keldysh action*

In this section we will introduce a new action functional. This functional does not suffer from the problems of the usual action. First of all the functional is not made stationary but merely used as a generating function for the density and the response functions. In this respect the function is very similar to the partition function of statistical mechanics.

In the definition of the new action functional we use the time contour method due to Keldysh⁵⁰ in which the physical time t is parametrized by an underlying parameter τ , called pseudotime. This procedure was originally introduced by Keldysh in order to obtain an elegant treatment of nonequilibrium systems in terms of many-body Green functions.^{50–54} We will use the same procedure in the definition of our action functional. Higher functional derivatives of the new action functional will lead to response functions which are symmetric in the Keldysh time contour parameter. Transforming back to physical time t then yields the desired causal, i.e., retarded response functions in terms of t .

The Keldysh contour is defined by parametrizing the physical time $t(\tau)$ in terms of a pseudotime τ in such a way that if τ runs from τ_i to τ_f then t runs from t_0 to \tilde{t} and from \tilde{t} back to t_0 . The value of \tilde{t} can be chosen arbitrarily as long as physical quantities are calculated at earlier times. In practice one often takes $\tilde{t} = +\infty$.⁵⁰ The actual form of the parametrization is irrelevant since the final results are independent of it. The initial state of the system at time t_0 is given by the wavefunction Ψ_0 . The evolution of this state in pseudotime is governed by the Schrödinger equation

$$(it'(\tau)^{-1}\partial_\tau - \hat{H}(\tau))|\Psi(\tau)\rangle = 0, \quad (182)$$

where $t'(\tau) = dt/d\tau$. The Hamiltonian $\hat{H}(\tau)$ is given by $\hat{H}(\tau) = \hat{T} + \hat{U}(\tau) + \hat{W}$ where \hat{T} represents the kinetic energy operator, \hat{U} the external field explicitly given by $\hat{U}(\tau) = \int d^3r \hat{n}(\mathbf{r})u(\mathbf{r}\tau)$ and \hat{W} represents the two-particle interaction. It is easily seen that this Schrödinger equation reduces to the usual one if $u(\mathbf{r}\tau)$ is equal on the forward and backward parts of the contour. The basic steps we will carry out here are similar to the ones in Sec. 2.2 with the difference that we will use a functional that is defined in terms of pseudo-time rather than physical time. The consequences of this difference will become clear soon. We first define a functional of the external field u by

$$\tilde{A}[u] = i \ln \langle \Psi_0 | V(\tau_f, \tau_i) | \Psi_0 \rangle, \quad (183)$$

where Ψ_0 is the initial state and where V is the τ - or contour ordered evolution operator of the system

$$V(\tau_f, \tau_i) = T_C \exp \left[-i \int_{\tau_i}^{\tau_f} d\tau t'(\tau) \hat{H}(\tau) \right], \quad (184)$$

where T_C denotes ordering in τ .⁵³ It is this redefinition of the time-ordering operator in addition to the introduction of the time-contour which makes the Keldysh approach applicable in nonequilibrium Green function theory.⁵³ It is clear that if the external potential is equal on the forward and backward parts of the contour, i.e., of the form $u(\mathbf{r}\tau) = v(\mathbf{r}t(\tau))$, then this evolution operator will become unity and \tilde{A} will become zero. Potentials of this type will be denoted as physical potentials. Functional derivatives however, can be nonzero for physical potentials. For

example the functional derivative of \tilde{A} with respect to u yields

$$\frac{\delta \tilde{A}}{\delta u(\mathbf{r}\tau)} = \frac{\langle \Psi_0 | V(\tau_f, \tau) \hat{n}(\mathbf{r}) V(\tau, \tau_i) | \Psi_0 \rangle}{\langle \Psi_0 | V(\tau_f, \tau_i) | \Psi_0 \rangle} = \langle \hat{n}_H(\mathbf{r}\tau) \rangle = n(\mathbf{r}\tau), \quad (185)$$

where we defined the Heisenberg representation of an operator \hat{O} in pseudo-time by $\hat{O}_H(\tau) = V(\tau_i, \tau) \hat{O} V(\tau, \tau_i)$ and the expectation value by

$$\langle \hat{O}_H(\tau) \rangle = \frac{\langle \Psi_0 | T_C[V(\tau_f, \tau_i) \hat{O}_H(\tau)] | \Psi_0 \rangle}{\langle \Psi_0 | V(\tau_f, \tau_i) | \Psi_0 \rangle}. \quad (186)$$

Note that we have adopted the usual convention of Keldysh–Green function theory⁵³ in which the functional derivative is defined by

$$\delta \tilde{A} = \int d^3r d\tau t'(\tau) \frac{\delta \tilde{A}}{\delta u(\mathbf{r}\tau)} \delta u(\mathbf{r}\tau), \quad (187)$$

i.e. the term $t'(\tau)$ belongs to the integration measure rather than the functional derivative. If we now evaluate the derivative of \tilde{A} at a physical potential $u(\mathbf{r}\tau) = v(\mathbf{r}t(\tau))$ we obtain

$$\left. \frac{\delta \tilde{A}}{\delta u(\mathbf{r}\tau)} \right|_{u=v(\mathbf{r}t)} = \langle \Psi_0 | V(t_0, t) \hat{n}(\mathbf{r}) V(t, t_0) | \Psi_0 \rangle = n(\mathbf{r}t), \quad (188)$$

where the operator V is now the usual evolution operator in physical time. Therefore, the derivative of \tilde{A} at the physical potential v is the density of the system in the external field v . As was pointed out in Sec. 2.2 it is not possible to construct a functional with this property if the density is restricted to be a function of physical time. We now want to use $n(\mathbf{r}\tau)$ as our basic variable and we perform a Legendre transform by defining

$$A[n] = -\tilde{A}[u] + \int_C dt d^3r n(\mathbf{r}\tau) u(\mathbf{r}\tau), \quad (189)$$

so that

$$\frac{\delta A}{\delta n(\mathbf{r}\tau)} = u(\mathbf{r}\tau). \quad (190)$$

For notational convenience we introduced the shortened notation $\int_C dt$ for $\int d\tau t'(\tau)$. The Legendre transformation assumes that there is a one-to-one relation between $u(\mathbf{r}\tau)$ and $n(\mathbf{r}\tau)$ so that Eq. (185) is invertible. This inverse is unique modulo a purely τ -dependent function $C(\tau)$. We will prove this in the next section for the case of perturbations from an initial ground state. Note further that

$$\tilde{A}[u + C(\tau)] = \tilde{A}[u] + N \int_C dt C(\tau), \quad (191)$$

where N is the number of particles in the system. This means that the arbitrariness with respect to adding a purely τ -dependent function to the potential cancels in the definition of $A[n]$ which makes $A[n]$ well-defined.

For a noninteracting system with the Hamiltonian

$$\hat{H}_s(\tau) = \hat{T} + \hat{U}_s(\tau), \quad (192)$$

we can now define the action functional

$$\tilde{A}_s[u_s] = i \ln \langle \Phi_0 | V_s(\tau_f, \tau_i) | \Phi_0 \rangle. \quad (193)$$

The evolution operator $V_s(\tau_f, \tau_i)$ is similar to the one in Eq. (184) and obtained by replacing \hat{H} by \hat{H}_s . The initial wavefunction Φ_0 at $t = t_0$ is a Slater determinant. We can now do a similar Legendre transform and define

$$A_s[n] = -\tilde{A}_s[u_s] + \int_C dt d^3r n(\mathbf{r}\tau) u_s(\mathbf{r}\tau). \quad (194)$$

The exchange-correlation part A_{xc} of the action functional is then defined by

$$A[n] = A_s[n] - A_{xc}[n] - \frac{1}{2} \int_C dt d^3r_1 d^3r_2 \frac{n(\mathbf{r}_1\tau) n(\mathbf{r}_2\tau)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (195)$$

The above equation implicitly assumes that the functionals A and A_s are defined on the same domain, i.e., that there exists a noninteracting system described by the Hamiltonian \hat{H}_s with the same density as the interacting system described by the Hamiltonian \hat{H} . For this to be true it is necessary that the initial states Ψ_0 and Φ_0 yield the same density. For most applications, Ψ_0 will be the ground state of the system before the time-dependent field is switched on and Φ_0 will be the corresponding Kohn–Sham determinant obtained from stationary density-functional theory. Functional differentiation of Eq. (195) with respect to $n(\mathbf{r}\tau)$ yields

$$u(\mathbf{r}\tau) = u_s(\mathbf{r}\tau) - u_{xc}(\mathbf{r}\tau) - u_H(\mathbf{r}\tau), \quad (196)$$

where the Hartree potential is $u_H(\mathbf{r}\tau) = \int d^3r' n(\mathbf{r}'\tau)/|\mathbf{r} - \mathbf{r}'|$ and where the exchange-correlation potential is formally defined by

$$u_{xc}(\mathbf{r}\tau) = \frac{\delta A_{xc}}{\delta n(\mathbf{r}\tau)}. \quad (197)$$

The above construction yields a potential u_s for a noninteracting system with the same density as the fully interacting system with potential u . The noninteracting system is thus to be identified with the time-dependent Kohn–Sham system. If we take the above derivatives at the physical time-dependent density $n(\mathbf{r}t)$ corresponding to the potential $u(\mathbf{r}\tau) = v(\mathbf{r}t(\tau))$ of the interacting system, we can transform again to physical time. The Kohn–Sham system is then given by the equations

$$\left[-\frac{1}{2} \nabla^2 + v(\mathbf{r}t) + v_H(\mathbf{r}t) + v_{xc}(\mathbf{r}t) \right] \phi_i(\mathbf{r}t) = i \partial_t \phi_i(\mathbf{r}t), \quad (198)$$

$$v_{xc}(\mathbf{r}t) = \left. \frac{\delta A_{xc}}{\delta n(\mathbf{r}\tau)} \right|_{n=n(\mathbf{r}t)},$$

where the density $n(\mathbf{r}t)$ can be calculated as the sum of the squares of the occupied orbitals. We now address the causality and symmetry properties associated with

the response functions, that have led to a paradox in an earlier version of time-dependent density functional theory. The second derivative of the functional \tilde{A} yields

$$\chi(\mathbf{r}_1\tau_1, \mathbf{r}_2\tau_2) = \frac{\delta^2 \tilde{A}}{\delta u(\mathbf{r}_1\tau_1)\delta u(\mathbf{r}_2\tau_2)} = -i\langle T_C \Delta \hat{n}_H(\mathbf{r}_1\tau_1) \Delta \hat{n}_H(\mathbf{r}_2\tau_2) \rangle, \quad (199)$$

where the density fluctuation operator $\Delta \hat{n}_H(\mathbf{r}\tau) = \hat{n}_H(\mathbf{r}\tau) - \langle \hat{n}_H(\mathbf{r}\tau) \rangle$ enters rather than the density operator, due to the derivatives of the denominator in Eq. (185). This density response function is symmetric as it should and from the Legendre transform it follows that its inverse is given by

$$\chi^{-1}(\mathbf{r}_1\tau_1, \mathbf{r}_2\tau_2) = \frac{\delta^2 A}{\delta n(\mathbf{r}_1\tau_1)\delta n(\mathbf{r}_2\tau_2)}. \quad (200)$$

Taking the second functional derivative of Eq. (195) now yields

$$\chi^{-1} = \chi_s^{-1} - \frac{1}{t'(\tau_1)} \frac{\delta(\tau_1 - \tau_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} - f_{xc}, \quad (201)$$

where χ_s^{-1} is the inverse of the Kohn–Sham density response function and

$$f_{xc}(\mathbf{r}_1\tau_1, \mathbf{r}_2\tau_2) = \frac{\delta v_{xc}(\mathbf{r}_1\tau_1)}{\delta n(\mathbf{r}_2\tau_2)}. \quad (202)$$

Since both χ^{-1} and χ_s^{-1} are symmetric also f_{xc} must be symmetric. However, these functions will become causal in physical time. In order to see how they act in physical time we calculate the density response $\delta n(\mathbf{r}t)$ due to a variation $\delta v(\mathbf{r}t)$. The function χ evaluated at a physical density $n(\mathbf{r}t)$ is given by

$$i\chi(\mathbf{r}_1\tau_1, \mathbf{r}_2\tau_2) = \theta(\tau_1 - \tau_2) \langle \Delta \hat{n}_H(\mathbf{r}_1\tau_1) \Delta \hat{n}_H(\mathbf{r}_2\tau_2) \rangle + (1 \leftrightarrow 2), \quad (203)$$

where the second term is identical to the first term with the indices interchanged. Hence, we have

$$\begin{aligned} \delta n(\mathbf{r}_1t_1) &= \int_C dt_2 d^3r_2 \chi(\mathbf{r}_1\tau_1, \mathbf{r}_2\tau_2) \delta v(\mathbf{r}_2t_2) \\ &= -i \int_{\tau_i}^{\tau_1} d\tau_2 t'(\tau_2) d^3r_2 \langle \Delta \hat{n}_H(\mathbf{r}_1\tau_1) \Delta \hat{n}_H(\mathbf{r}_2\tau_2) \rangle \delta v(\mathbf{r}_2t_2) \\ &\quad - i \int_{\tau_1}^{\tau_f} d\tau_2 t'(\tau_2) d^3r_2 \langle \Delta \hat{n}_H(\mathbf{r}_2\tau_2) \Delta \hat{n}_H(\mathbf{r}_1\tau_1) \rangle \delta v(\mathbf{r}_2t_2) \\ &= \int_{t_0}^{+\infty} dt_2 d^3r_2 \chi_R(\mathbf{r}_1t_1, \mathbf{r}_2t_2) \delta v(\mathbf{r}_2t_2), \end{aligned} \quad (204)$$

where

$$i\chi_R(\mathbf{r}_1t_1, \mathbf{r}_2t_2) = \theta(t_1 - t_2) \langle \Psi_0 | [\hat{n}_H(\mathbf{r}_1t_1), \hat{n}_H(\mathbf{r}_2t_2)] | \Psi_0 \rangle. \quad (205)$$

In the last step we used that the expectation value of the commutator of the density fluctuation operators is equal to the expectation value of the commutator of the

density operators themselves. In a similar fashion for χ_s we obtain $\chi_{s,R}$ which is given by Eq. (205) with Ψ_0 replaced by Φ_0 . From Eq. (201) we see that f_{xc} has a structure similar to χ and χ_s . Transformation to physical time yields the causal equivalent $f_{xc,R}$. Acting in physical time, Eq. (201) then becomes

$$\chi_R^{-1} = \chi_{s,R}^{-1} - \frac{\delta(t_1 - t_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} - f_{xc,R}. \quad (206)$$

This is the basic equation which is used to calculate excitation energies within TDDFT.^{46,47} We have thus obtained the main result of this section. All response functions, i.e. higher order derivatives of the action functional are symmetric functions in pseudotime and become causal functions when transformed back to physical time. This resolves the paradox arising from the previous definition of the action functional.

We will now discuss a useful application of the new formalism, namely a new derivation of the time-dependent optimized potential method (TDOPM).⁵⁵

The exchange-correlation part A_{xc} of the action functional can be expanded in terms of Keldysh–Green functions⁵⁶ where the perturbing Hamiltonian is given by $\hat{H} - \hat{H}_s$. The expansion of the logarithm of the evolution operator yields the set of closed connected diagrams. Perturbation theory in addition requires an adiabatic switching-on of $\hat{H} - \hat{H}_s$ in the physical time interval $(-\infty, t_0)$ in order to connect the states Ψ_0 and Φ_0 . This is however readily achieved by extending the Keldysh contour to $-\infty$.⁵⁶ If we restrict the derivation to the first order terms we find that the Hartree term and the term with $u - u_s$ cancel, and thus we obtain the exchange-only expression

$$A_x[n] = -\frac{1}{2} \sum_{ij}^N \int_C dt d^3r_1 d^3r_2 \frac{\phi_i^*(\mathbf{r}_1\tau) \phi_i(\mathbf{r}_2\tau) \phi_j(\mathbf{r}_1\tau) \phi_j^*(\mathbf{r}_2\tau)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (207)$$

One sees that this functional is an implicit functional of $n(\mathbf{r}\tau)$ but an explicit functional of the orbitals. Going to higher order in $\hat{H} - \hat{H}_s$, the Keldysh perturbation expansion leads to orbital dependent expressions for the correlation part A_c of the action. In that case one may obtain u_{xc} from

$$u_{xc}(\mathbf{r}_2\tau_2) = \int_C dt d^3r_1 \frac{\delta A_{xc}}{\delta u_s(\mathbf{r}_1\tau_1)} \frac{\delta u_s(\mathbf{r}_1\tau_1)}{\delta n(\mathbf{r}_2\tau_2)}. \quad (208)$$

Multiplication by χ_s and use of the chain rule for differentiation yields

$$\begin{aligned} & \int_C dt_2 d^3r_2 \chi_s(\mathbf{r}_1\tau_1, \mathbf{r}_2\tau_2) u_{xc}(\mathbf{r}_2\tau_2) \\ &= \sum_{i=1}^N \int_C dt_2 d^3r_2 \frac{\delta A_{xc}}{\delta \phi_i(\mathbf{r}_2\tau_2)} \frac{\delta \phi_i(\mathbf{r}_2\tau_2)}{\delta u_s(\mathbf{r}_1\tau_1)} + \frac{\delta A_{xc}}{\delta \phi_i^*(\mathbf{r}_2\tau_2)} \frac{\delta \phi_i^*(\mathbf{r}_2\tau_2)}{\delta u_s(\mathbf{r}_1\tau_1)}. \end{aligned} \quad (209)$$

Now we work out some terms on the right hand side of this equation. In the following we will only consider the realistic case where the functional derivative $\delta A_{xc}/\delta \phi_i^*$ at a physical potential is the complex conjugate of $\delta A_{xc}/\delta \phi_i$. Calculating the functional

derivatives $\delta\phi_i/\delta u_s$ and $\delta\phi_i^*/\delta u_s$ requires careful consideration of the boundary conditions. From Eq. (193) it follows that the state $|\Phi_0\rangle$ evolves from τ_i forward in pseudotime and therefore the variations $\delta\phi_i$ have to satisfy the boundary condition $\delta\phi_i(\tau_i) = 0$. However, the complex conjugate state $\langle\Phi_0|$ evolves from τ_f backwards in pseudotime and thus the variations $\delta\phi_i^*$ have to satisfy the boundary condition $\delta\phi_i^*(\tau_f) = 0$. Carrying out these variations in a similar way as in Ref. 55 we obtain from the pseudotime Kohn–Sham equations

$$\begin{aligned}\frac{\delta\phi_i(\mathbf{r}_2\tau_2)}{\delta u_s(\mathbf{r}_1\tau_1)} &= -i\theta(\tau_2 - \tau_1)\phi_i(\mathbf{r}_1\tau_1)\sum_j\phi_j(\mathbf{r}_2\tau_2)\phi_j^*(\mathbf{r}_1\tau_1), \\ \frac{\delta\phi_i^*(\mathbf{r}_2\tau_2)}{\delta u_s(\mathbf{r}_1\tau_1)} &= -i\theta(\tau_1 - \tau_2)\phi_i^*(\mathbf{r}_1\tau_1)\sum_j\phi_j^*(\mathbf{r}_2\tau_2)\phi_j(\mathbf{r}_1\tau_1).\end{aligned}\quad (210)$$

Inserting the above expressions and transforming back to physical time yields the integral equation

$$\begin{aligned}\sum_j^N\int dt_2 d^3r_2 G_R(\mathbf{r}_1t_1, \mathbf{r}_2t_2)\phi_j(\mathbf{r}_1t_1)\phi_j^*(\mathbf{r}_2t_2) \\ \times [v_{xc}(\mathbf{r}_2t_2) - w_{xcj}(\mathbf{r}_2t_2)] + \text{c.c.} = 0,\end{aligned}\quad (211)$$

where we defined the retarded Green function by

$$iG_R(\mathbf{r}_1t_1, \mathbf{r}_2t_2) = \theta(t_1 - t_2)\sum_j\phi_j^*(\mathbf{r}_1t_1)\phi_j(\mathbf{r}_2t_2)\quad (212)$$

and the quantity w_{xcj} by

$$w_{xcj}(\mathbf{r}t) = \frac{1}{\phi_j^*(\mathbf{r}t)}\left.\frac{\delta A_{xc}}{\delta\phi_j(\mathbf{r}\tau)}\right|_{\phi_i=\phi_i(\mathbf{r}t)}.\quad (213)$$

The Eq. (211) is the well known equation of the TDOPM.⁵⁵

The results of this section can be summarized as follows: We have resolved an existing paradox regarding the causality and symmetry properties of response functions within TDDFT. This is achieved by introducing an action functional defined on a Keldysh contour. From this action we furthermore derived the time-dependent Kohn–Sham equations and, as example, the TDOPM equations.

4.3. *Invertability proof for the Keldysh linear response function*

In the previous section we derived the time-dependent Kohn–Sham equations from an action principle. In this derivation it was assumed that there is a one-to-one relation between the contour density $n(\mathbf{r}\tau)$ and the contour potential $u(\mathbf{r}\tau)$. In this section we will investigate this point more closely.

As a first guess one may think that the one-to-one relation between contour density and potential can be proven along the same lines as in the usual Runge–Gross proof. However, one soon realizes that this is not the case. The Runge–Gross

proof is based on a Taylor expansion of the potential and the density around the initial time t_0 , where one uses the fact that one can calculate the expectation values at $t = t_0$ from the initial state wavefunction. However, in the Keldysh formulation the contour quantities at the endpoints of the contour do not depend just on the initial state. For instance, for the contour density at $\tau = \tau_i$ one has:

$$n(\mathbf{r}\tau_i) = \frac{\langle \Psi_0 | V(\tau_f, \tau_i) \hat{n}(\mathbf{r}) | \Psi_0 \rangle}{\langle \Psi_0 | V(\tau_f, \tau_i) | \Psi_0 \rangle}. \quad (214)$$

We see that this quantity does not only depend on the initial state $|\Psi_0\rangle$, but also on the complete evolution of this state along the contour, which is governed by the evolution operator $V(\tau_f, \tau_i)$. Only for potentials that are identical on the forward and backward part of the contour this evolution operator becomes equal to the identity operator in which case the fully evolved state has returned exactly to the initial state. We therefore see that the Runge–Gross proof can not be generalized in a straightforward way to the contour case. The same is true for the extended Runge–Gross proof of Sec. 2.5. For this reason we set ourselves a more modest goal and will instead prove that the Keldysh linear response function is invertable.

We consider the ground state $|\Psi_0\rangle$ of a many-body Hamiltonian \hat{H} . Then we add an additional potential $\phi(\mathbf{r}\tau)$ where $\tau_i \leq \tau \leq \tau_f$ and solve for the forward solution

$$|\Psi_i(\tau)\rangle = V(\tau, \tau_i) |\Psi_0\rangle \quad (215)$$

and for the backward solution

$$\langle \Psi_f(\tau) | = \langle \Psi_0 | V(\tau_f, \tau) \quad (216)$$

of the contour Schrödinger equation (182) with the boundary condition $|\Psi_i(\tau_i)\rangle = |\Psi_0\rangle$ and $\langle \Psi_f(\tau_f) | = \langle \Psi_0 |$. From this we obtain the contour density

$$n(\mathbf{r}\tau) = \frac{\langle \Psi_f(\tau) | \hat{n}(\mathbf{r}) | \Psi_i(\tau) \rangle}{\langle \Psi_f(\tau) | \Psi_i(\tau) \rangle}. \quad (217)$$

This yields a density variation $\delta n(\mathbf{r}\tau) = n(\mathbf{r}\tau) - n_0(\mathbf{r})$, where $n_0(\mathbf{r})$ is the density of ground state $|\Psi_0\rangle$. We will show that zero density variations can only be reproduced by potentials of the form $\phi(\mathbf{r}\tau) = C(\tau)$, i.e. purely τ -dependent functions. In order to prove this we start out from the Keldysh linear response function:

$$\begin{aligned} i\chi(\mathbf{r}_1\tau_1, \mathbf{r}_2\tau_2) &= \theta(\tau_1 - \tau_2) \langle \Psi_0 | \Delta \hat{n}_H(\mathbf{r}_1\tau_1) \Delta \hat{n}_H(\mathbf{r}_2\tau_2) | \Psi_0 \rangle \\ &\quad + \theta(\tau_2 - \tau_1) \langle \Psi_0 | \Delta \hat{n}_H(\mathbf{r}_2\tau_2) \Delta \hat{n}_H(\mathbf{r}_1\tau_1) | \Psi_0 \rangle. \end{aligned} \quad (218)$$

The density response can be written as

$$\delta n(\mathbf{r}\tau) = \delta n^>(\mathbf{r}\tau) + \delta n^<(\mathbf{r}\tau), \quad (219)$$

where

$$\delta n^>(\mathbf{r}_1\tau_1) = -i \int_{\tau_i}^{\tau_1} d\tau_2 \tau'(\tau_2) \int d^3r_2 \langle \Psi_0 | \Delta \hat{n}_H(\mathbf{r}_1\tau_1) \Delta \hat{n}_H(\mathbf{r}_2\tau_2) | \Psi_0 \rangle \phi(\mathbf{r}_2\tau_2) \quad (220)$$

and

$$\delta n^<(\mathbf{r}_1\tau_1) = -i \int_{\tau_1}^{\tau_f} d\tau_2 t'(\tau_2) \int d^3 r_2 \langle \Psi_0 | \Delta \hat{n}_H(\mathbf{r}_2 t_2) \Delta \hat{n}_H(\mathbf{r}_1 t_1) | \Psi_0 \rangle \phi(\mathbf{r}_2 \tau_2) \quad (221)$$

with the above definitions we find immediately that

$$(\delta n^<(\mathbf{r}_1\tau_1))^* = \delta n^>(\mathbf{r}_1\tau_1) + \nu(\mathbf{r}_1 t_1), \quad (222)$$

where we defined

$$\nu(\mathbf{r}_1 t_1) = i \int_{\tau_i}^{\tau_f} d\tau_2 t'(\tau_2) \int d^3 r_2 \langle \Psi_0 | \Delta \hat{n}_H(\mathbf{r}_1 t_1) \Delta \hat{n}_H(\mathbf{r}_2 t_2) | \Psi_0 \rangle \phi(\mathbf{r}_2 \tau_2). \quad (223)$$

We therefore have

$$\delta n(\mathbf{r}\tau) = 2 \operatorname{Re}(\delta n^<(\mathbf{r}\tau)) - \nu(\mathbf{r}t). \quad (224)$$

Because of the term ν the contour density response δn is in general a complex quantity. We first show that $\delta n = 0$ implies that $\nu = 0$. From the above equation we see immediately that $\delta n = 0$ implies that $\operatorname{Im}(\nu) = 0$. Now

$$\begin{aligned} 2i \operatorname{Im}(\nu(\mathbf{r}_1 t_1)) &= \nu(\mathbf{r}_1 t_1) - \nu^*(\mathbf{r}_1 t_1) \\ &= i \langle \Psi_0 | \Delta \hat{n}_H(\mathbf{r}_1 t_1) \hat{\Phi} | \Psi_0 \rangle + i \langle \Psi_0 | \hat{\Phi} \Delta \hat{n}_H(\mathbf{r}_1 t_1) | \Psi_0 \rangle, \end{aligned} \quad (225)$$

where we defined the Hermitian operator

$$\hat{\Phi} = \int_{\tau_i}^{\tau_f} d\tau t'(\tau) \int d^3 r \hat{n}_H(\mathbf{r}t) \phi(\mathbf{r}\tau). \quad (226)$$

Multiplying Eq. (225) by ϕ and integrating over \mathbf{r}_1 and τ_1 yields

$$\int_{\tau_i}^{\tau_f} d\tau_1 t'(\tau_1) \int d^3 r_1 \operatorname{Im}(\nu(\mathbf{r}_1 t_1)) \phi(\mathbf{r}_1 \tau_1) = \langle \Psi_0 | \hat{\Phi} \hat{\Phi} | \Psi_0 \rangle. \quad (227)$$

Therefore $\operatorname{Im}(\nu) = 0$ implies that

$$0 = \langle \Psi_0 | \hat{\Phi} \hat{\Phi} | \Psi_0 \rangle = \langle \Psi_0 | \hat{\Phi}^\dagger \hat{\Phi} | \Psi_0 \rangle, \quad (228)$$

where we used that $\hat{\Phi}$ is Hermitian. This equation implies immediately that the norm of $\hat{\Phi}|\Psi_0\rangle$ is zero and thus that $\hat{\Phi}|\Psi_0\rangle = 0$ and therefore

$$\nu(\mathbf{r}t) = i \langle \Psi_0 | \hat{n}_H(\mathbf{r}t) \hat{\Phi} | \Psi_0 \rangle = 0. \quad (229)$$

We have therefore shown that $\delta n = 0$ implies $\nu = 0$ and therefore also $\operatorname{Re}(\delta n^>) = \operatorname{Re}(\delta n^<) = 0$. Now we can parametrize $\phi(\mathbf{r}\tau)$ by two functions of $t(\tau)$ on the upper and lower part of the Keldysh contour, i.e.:

$$\phi(\mathbf{r}\tau) = \begin{cases} u_1(\mathbf{r}t(\tau)), & (\tau_i \leq \tau \leq \tau_0), \\ u_2(\mathbf{r}t(\tau)), & (\tau_0 \leq \tau \leq \tau_f). \end{cases} \quad (230)$$

Now the condition $\operatorname{Re}(\delta n^>) = 0$ for $\tau_i \leq \tau \leq \tau_0$ yields in the real time interval $t_0 \leq t \leq \tilde{t}$ the condition

$$0 = -i \int_{t_0}^{\tilde{t}} dt_2 \int d^3 r_2 \langle \Psi_0 | [\Delta \hat{n}_H(\mathbf{r}_1 t_1), \Delta \hat{n}_H(\mathbf{r}_2 t_2)] | \Psi_0 \rangle u_1(\mathbf{r}_2 t_2). \quad (231)$$

One should remember that the turning point \tilde{t} of the Keldysh contour can be taken to be infinitely large and therefore t_1 is an arbitrary time between t_0 and infinity. The analogous condition $\text{Re}(\delta n^<) = 0$ for $\tau_0 \leq \tau \leq \tau_f$ yields an identical equation to Eq. (231) with u_1 replaced by u_2 . The above equation is however just the linear response function in physical time, for which we already proved invertability (see Sec. 3.2). We therefore find that, if $\delta n = 0$, then u_1 and u_2 can only be equal to purely time-dependent functions. Hence the Keldysh response function can only yield zero response for perturbations of the form $\phi(\mathbf{r}\tau) = C(\tau)$. This proves the invertability of the Keldysh response function.

4.4. An illustrative example

The derivations based on the Keldysh action principle were thusfar rather general and abstract. We therefore want to show how the formalism works in a simple example that can be solved exactly, namely the quantum version of the forced harmonic oscillator.⁵⁷ The Schrödinger equation for this problem is given by:

$$-\frac{1}{2}\partial_x^2\Psi(xt) + \left(\frac{1}{2}x^2 - xF(t)\right)\Psi(xt) = i\partial_t\Psi(xt) \quad (232)$$

where initial wavefunction is given at $t = t_0$ by $\Psi(xt_0) = \Psi_0(x)$. In this equation the function $F(t)$ is an arbitrary time-dependent force. Given the initial state there is, as we will show, a one-to-one relation between the expectation value of position $\langle x(t) \rangle$ and the applied force $F(t)$. To illustrate the Keldysh formalism we will first define a functional of the external force and we will then construct a functional of the expectation value of position by the method of Legendre transforms.

In the Keldysh approach one defines a time-contour $t(\tau)$ that runs from $t(\tau_i) = t_0$ to some time t_1 and then back to $t(\tau_f) = t_0$. The physical time interval from t_0 to t_1 is thus parametrized by a pseudo-time variable running from τ_i to τ_f . In order to derive quantities from an action functional one needs to make variations in the potential which are different on the forward and backward parts of the contour. One therefore needs variations in the potential that are general functions of τ rather than functions of $t(\tau)$. In order to do this we generalize the Schrödinger equation to:

$$-\frac{1}{2}\partial_x^2\Psi(x\tau) + \left[\frac{1}{2}x^2 - xF(\tau)\right]\Psi(x\tau) = i\frac{1}{t'(\tau)}\partial_\tau\Psi(x\tau), \quad (233)$$

where $t'(\tau) = dt/d\tau$. The external force $F(\tau)$ is now a general function of τ rather than a function of $t(\tau)$. The force $F(\tau)$ and the position x are conjugate variables in the Schrödinger equation. This is analogous to the potential $u(\mathbf{r}\tau)$ and density $n(\mathbf{r}\tau)$ which are conjugate variables in the many-body Hamiltonian. We therefore start out by defining a functional of the external force $F(\tau)$ by

$$\tilde{A}[F] = i \ln \langle \Psi_0 | V(\tau_f, \tau_i) | \Psi_0 \rangle, \quad (234)$$

where V is the τ -ordered evolution operator of the system:

$$V(\tau_f, \tau_i) = T_C \exp \left[-i \int_{\tau_i}^{\tau_f} d\tau t'(\tau) \hat{H}(\tau) \right]. \quad (235)$$

Here T_C denotes ordering in τ and \hat{H} is the Hamiltonian of the forced harmonic oscillator. Functional differentiation of \tilde{A} with respect to F yields the expectation value of the position operator

$$-\frac{\delta \tilde{A}}{\delta F(\tau)} = \frac{\langle \Psi_0 | V(\tau_f, \tau) x V(\tau, \tau_i) | \Psi_0 \rangle}{\langle \Psi_0 | V(\tau_f, \tau_i) | \Psi_0 \rangle} = \langle x_H(\tau) \rangle, \quad (236)$$

whereas the second derivative yields a response function

$$-\frac{\delta^2 \tilde{A}}{\delta F(\tau') \delta F(\tau)} = \frac{\delta \langle x_H(\tau) \rangle}{\delta F(\tau')} = -i \langle T_C \Delta x_H(\tau) \Delta x_H(\tau') \rangle \quad (237)$$

where $\Delta x_H(\tau) = x_H(\tau) - \langle x_H(\tau) \rangle$. If we introduce the notation $X(\tau) = \langle x_H(\tau) \rangle$ we can define the Legendre transform of \tilde{A} by

$$A[X] = -\tilde{A}[F] - \int_C dt X(\tau) F(\tau), \quad (238)$$

with functional derivative

$$\frac{\delta A}{\delta X(\tau)} = -F(\tau). \quad (239)$$

In the following we will calculate all of the above quantities explicitly. For notational convenience we first introduce the notation:

$$\dot{f}(\tau) = \frac{1}{t'(\tau)} \partial_\tau f(\tau), \quad (240)$$

$$\ddot{f}(\tau) = \frac{1}{t'(\tau)} \partial_\tau \left(\frac{1}{t'(\tau)} \partial_\tau f(\tau) \right). \quad (241)$$

The initial state is taken to be the ground state of the harmonic oscillator

$$\Psi_0(x) = \pi^{-1/4} \exp \left(-\frac{1}{2} x^2 \right). \quad (242)$$

The ground state energy is $E_0 = 1/2$. The full solution of the forward solution with boundary condition $\Psi(\tau_i) = \Psi_0$ is:

$$\Psi_i(x\tau) = \pi^{-1/4} \exp \left[-\frac{1}{2} (x - v_i(\tau))^2 + ix\dot{v}_i(\tau) - i \int_{\tau_i}^{\tau} d\bar{\tau} t'(\bar{\tau}) \left(\frac{1}{2} + S_i(\bar{\tau}) \right) \right], \quad (243)$$

where $v_i(\tau)$ is the solution of the equation

$$\ddot{v}_i(\tau) + v_i(\tau) = F(\tau), \quad (244)$$

with the boundary conditions

$$v_i(\tau_i) = \dot{v}_i(\tau_i) = 0. \quad (245)$$

The function $S_i(\tau)$ is given by

$$S_i(\tau) = \frac{1}{2}(\dot{v}_i^2(\tau) - v_i^2(\tau)) \quad (246)$$

and corresponds to the classical action of an harmonic oscillator. The explicit solution of Eq. (244) with boundary conditions (245) is given by

$$v_i(\tau) = \int_{\tau_i}^{\tau} d\bar{\tau} t'(\bar{\tau}) \sin(t(\tau) - t(\bar{\tau})) F(\bar{\tau}). \quad (247)$$

Now we consider the backward solution which evolves from initial state Ψ_0 at τ_f backwards in pseudotime. This solution is, of course, described by the same equations as above. We only have to change the subindex i to f . This procedure leads for instance to the following expression for the quantity $v_f(\tau)$:

$$v_f(\tau) = \int_{\tau_f}^{\tau} d\bar{\tau} t'(\bar{\tau}) \sin(t(\tau) - t(\bar{\tau})) F(\bar{\tau}). \quad (248)$$

Note that τ_f occurs in the lower limit of the integral although $\tau \leq \tau_f$. Interchanging the boundaries of the integration interval changes of sign of the integral. In order to evaluate the action we first calculate the expectation value of the evolution operator

$$\varepsilon(\tau_f, \tau_i) = \langle \Psi_0 | V(\tau_f, \tau_i) | \Psi_0 \rangle. \quad (249)$$

There are several ways to calculate this quantity. One way is to evolve the state Ψ_i to $\tau = \tau_f$ and to project on the initial state Ψ_0 , i.e.

$$\varepsilon(\tau_f, \tau_i) = \int_{-\infty}^{+\infty} dx \Psi_0^*(x) \Psi_i(x\tau_f). \quad (250)$$

This yields

$$\varepsilon = \exp \left[-i \int_{\tau_i}^{\tau_f} d\tau t'(\tau) S_i(\tau) - \frac{1}{4}(\dot{v}_i^2(\tau_f) + \dot{v}_i^2(\tau_i)) + \frac{i}{2} v_i(\tau_f) \dot{v}_i(\tau_f) \right]. \quad (251)$$

We therefore find for the action $\tilde{A} = i \ln \varepsilon$ the following expression

$$\tilde{A}[F] = \int_{\tau_i}^{\tau_f} d\tau t'(\tau) S_i(\tau) - \frac{1}{2} v_i(\tau_f) \dot{v}_i(\tau_f) - \frac{i}{4} [\dot{v}_i^2(\tau_f) + \dot{v}_i^2(\tau_i)], \quad (252)$$

which is just a classical action of an harmonic oscillator plus some boundary terms. It is also easily seen that this action is zero for a driving force that is equal on the forward and backward parts of the contour.

Let us further calculate some other expectation values. We calculate

$$\langle \Psi_0 | V(\tau_f, \tau) x V(\tau, \tau_i) | \Psi_0 \rangle = \int_{-\infty}^{+\infty} dx \Psi_f^*(x\tau) x \Psi_i(x\tau). \quad (253)$$

We find

$$\begin{aligned} X(\tau) &= \frac{\langle \Psi_0 | V(\tau_f, \tau) x V(\tau, \tau_i) | \Psi_0 \rangle}{\langle \Psi_0 | V(\tau_f, \tau_i) | \Psi_0 \rangle} \\ &= \frac{1}{2} (v_i(\tau) + v_f(\tau)) + \frac{i}{2} (\dot{v}_i(\tau) - \dot{v}_f(\tau)). \end{aligned} \quad (254)$$

This is more compactly written as

$$X(\tau) = \frac{i}{2} \int_{\tau_i}^{\tau} d\bar{\tau} t'(\bar{\tau}) e^{-i(t(\tau) - t(\bar{\tau}))} F(\bar{\tau}) + \frac{i}{2} \int_{\tau}^{\tau_f} d\bar{\tau} t'(\bar{\tau}) e^{i(t(\tau) - t(\bar{\tau}))} F(\bar{\tau}). \quad (255)$$

Note that $X(\tau)$ satisfies the differential equation

$$\ddot{X}(\tau) + X(\tau) = F(\tau) \quad (256)$$

with boundary conditions

$$\begin{aligned} \dot{X}(\tau_i) - iX(\tau_i) &= 0, \\ \dot{X}(\tau_f) + iX(\tau_f) &= 0. \end{aligned} \quad (257)$$

We see that since we have a second order differential equation for a complex function $X(\tau)$ we need two complex boundary conditions. From the differential equation for $X(\tau)$ we readily see that two different forces $F_1(\tau) \neq F_2(\tau)$ can not give the same $X(\tau)$. This establishes the one-to-one relation between the force $F(\tau)$ and pseudotime position $X(\tau)$. For a physical potential of the form $F(\tau) = E(t(\tau))$ we have $X(\tau) = v_i(\tau) = v_f(\tau) = u(t(\tau))$ where $u(t)$ is explicitly given by

$$u(t) = \int_{t_0}^t d\bar{t} \sin(t - \bar{t}) E(\bar{t}) \quad (258)$$

and satisfies the boundary conditions $u(t_0) = 0$ and $du/dt(t_0) = 0$.

Let us now calculate $X(\tau)$ from the action \tilde{A} . Using

$$\frac{\delta v_i(\tau)}{\delta F(\bar{\tau})} = \theta(\tau - \bar{\tau}) \sin(t(\tau) - t(\bar{\tau})), \quad (259)$$

$$\frac{\delta \dot{v}_i(\tau)}{\delta F(\bar{\tau})} = \theta(\tau - \bar{\tau}) \cos(t(\tau) - t(\bar{\tau})), \quad (260)$$

we can differentiate the action and we obtain

$$-\frac{\delta \tilde{A}}{\delta F(\tau)} = \frac{1}{2}(v_i(\tau) + v_f(\tau)) + \frac{i}{2}(\dot{v}_i(\tau) - \dot{v}_f(\tau)) = X(\tau). \quad (261)$$

The right hand side of this equation is indeed exactly the quantity $X(\tau)$ calculated before in Eq. (254). It should be remembered that the term $t'(\tau)$ belongs to the volume element rather than the functional derivative. Let us now calculate the linear response function:

$$\chi(\tau, \bar{\tau}) = -i \langle T_C \Delta x(\tau) \Delta x(\bar{\tau}) \rangle = \frac{\delta X(\tau)}{\delta F(\bar{\tau})}. \quad (262)$$

From the expression for $X(\tau)$ we immediately find

$$\chi(\tau, \bar{\tau}) = \theta(\tau - \bar{\tau}) \frac{i}{2} \exp[-i(t(\tau) - t(\bar{\tau}))] + \theta(\bar{\tau} - \tau) \frac{i}{2} \exp[-i(t(\bar{\tau}) - t(\tau))]. \quad (263)$$

This function is symmetric in τ and $\bar{\tau}$ as it should. Let us investigate the causality properties of the response function and calculate the response of $X(\tau)$ due to a physical perturbation $F(\tau) = E(t(\tau))$. Then

$$\begin{aligned}
 \delta u(t(\tau)) &= \delta X(\tau) = -i \int_{\tau_i}^{\tau_f} d\bar{\tau} t'(\bar{\tau}) \langle T_C \Delta x(\tau) \Delta x(\bar{\tau}) \rangle E(t(\bar{\tau})) \\
 &= \frac{1}{2} \int_{\tau_i}^{\tau} d\bar{\tau} t'(\bar{\tau}) [\sin(t(\tau) - t(\bar{\tau})) + i \cos(t(\tau) - t(\bar{\tau}))] E(t(\bar{\tau})) \\
 &\quad + \frac{1}{2} \int_{\tau}^{\tau_f} d\bar{\tau} t'(\bar{\tau}) [\sin(t(\bar{\tau}) - t(\tau)) + i \cos(t(\bar{\tau}) - t(\tau))] E(t(\bar{\tau})) \\
 &= \frac{1}{2} \int_{t_0}^t d\bar{t} [\sin(t - \bar{t}) + i \cos(t - \bar{t})] E(\bar{t}) \\
 &\quad - \frac{1}{2} \int_{t_0}^t d\bar{t} [\sin(\bar{t} - t) + i \cos(\bar{t} - t)] E(\bar{t}) \\
 &= \int_{t_0}^t d\bar{t} \sin(t - \bar{t}) E(\bar{t}) = -i \int_{t_0}^{\infty} \chi_R(t, \bar{t}) E(\bar{t}), \tag{264}
 \end{aligned}$$

where the retarded response function is given by

$$i\chi_R(t, \bar{t}) = \theta(t - \bar{t}) \langle [x_H(t), x_H(\bar{t})] \rangle = -\theta(t - \bar{t}) \sin(t - \bar{t}). \tag{265}$$

Note that the commutator of the Heisenberg representation of the position operator x_H is equal to the commutator of the Heisenberg representation of the position fluctuation operator Δx_H , i.e.

$$\langle [x_H(t), x_H(\bar{t})] \rangle = \langle [\Delta x_H(t), \Delta x_H(\bar{t})] \rangle. \tag{266}$$

From Eq. (255) it follows that the linear relation between $X(\tau)$ and $F(\tau)$ is exact, and not only valid in linear response. We have the exact relation

$$X(\tau) = \int_C d\bar{t} \chi(\tau, \bar{\tau}) F(\bar{\tau}). \tag{267}$$

This also means that for this particular problem all higher order response functions are zero. Another consequence is that the functional $\tilde{A}[F]$ is a quadratic functional of F and we readily find that

$$\tilde{A}[F] = -\frac{1}{2} \int_C dt \int_C d\bar{t} F(\tau) \chi(\tau, \bar{\tau}) F(\bar{\tau}). \tag{268}$$

In combination with Eq. (267) and the definition of the Legendre transform we see that

$$A[X] = -\frac{1}{2} \int_C dt F(\tau) X(\bar{\tau}), \tag{269}$$

where F has to be interpreted as a functional of X . With the equation of motion of $X(\tau)$ this yields

$$A[X] = -\frac{1}{2} \int_C dt (\ddot{X}(\tau) + X(\tau))X(\tau), \quad (270)$$

which can be rewritten as

$$A[X] = \frac{1}{2} \int_C dt (\dot{X}(\tau)^2 - X(\tau)^2) - \frac{1}{2} [X(\tau)\dot{X}(\tau)]_{\tau_i}^{\tau_f}. \quad (271)$$

This functional resembles the action of a classical harmonic oscillator. If we make variations δX we obtain after partial integration the variation in the action

$$\delta A = - \int_C dt (\ddot{X}(\tau) + X(\tau))\delta X(\tau) + \frac{1}{2} [\dot{X}(\tau)\delta X(\tau) - X(\tau)\delta \dot{X}(\tau)]_{\tau_i}^{\tau_f}. \quad (272)$$

Now the constraint must be incorporated that δX is a v -representable variation. This means that δX is determined from

$$\delta \ddot{X}(\tau) + \delta X(\tau) = \delta F(\tau) \quad (273)$$

for some perturbation δF . Moreover we must incorporate that the perturbed system evolves from the same initial state Ψ_0 as the unperturbed state. This implies that we must have the boundary conditions $\delta \Psi_i(\tau_i) = \delta \Psi_f(\tau_f) = 0$. These conditions on the wavefunctions imply that δX satisfies

$$\begin{aligned} \delta \dot{X}(\tau_i) - i\delta X(\tau_i) &= 0, \\ \delta \dot{X}(\tau_f) + i\delta X(\tau_f) &= 0. \end{aligned} \quad (274)$$

With the above boundary conditions we find that

$$\delta A = - \int_C dt F(\tau)\delta X(\tau) \quad (275)$$

implies

$$\begin{aligned} 0 &= \int_C dt [F(\tau) - \ddot{X}(\tau) - X(\tau)]\delta X(\tau) \\ &+ \frac{1}{2} [\dot{X}(\tau_f) + iX(\tau_f)]\delta X(\tau_f) - \frac{1}{2} [\dot{X}(\tau_i) - iX(\tau_i)]\delta X(\tau_i). \end{aligned} \quad (276)$$

This equation is obviously satisfied for arbitrary v -representable variations if X satisfies

$$\ddot{X}(\tau) + X(\tau) = F(\tau), \quad (277)$$

$$\dot{X}(\tau_i) - iX(\tau_i) = 0, \quad (278)$$

$$\dot{X}(\tau_f) + iX(\tau_f) = 0. \quad (279)$$

It is not obvious that there are not more solutions. However, expressing δX explicitly in terms of δF one can convince oneself that the only variational possibility

is presented by these equations. It is important to note that the variational equations yield both the equations of motion and the boundary conditions. This must of course be the case since the initial state is explicitly included in the definition of the action. The main point we learn from this example is that initial state and v -representability conditions must be used in order to derive the variational equations.

5. Conclusions and Outlook

In this review we presented an overview of the underlying principles of time-dependent density functional theory. We showed that one can transform the problem of interacting particles in a time-dependent field into an equivalent problem of non-interacting particles in an effective field, known as the Kohn–Sham potential. This transformation is based on a fundamental one-to-one relation between the external potential and the density of the system. This one-to-one relation was discussed in detail and we studied its dependence on the initial state. It was found that one can actually construct the potential from the density and the initial states, using the equations of motion. This construction also elucidates the initial state dependence of time-dependent density functionals.

We further showed how to calculate response properties and excitation energies from the time-dependent Kohn–Sham equations and proved invertability of the response function for switch-on potentials. This proof is valid for a larger class of potentials than allowed in the Runge–Gross proof and is a new result. In order to solve the Kohn–Sham response equations in practice approximate functionals for the exchange–correlation potential v_{xc} and the exchange–correlation kernel f_{xc} must be used. As a guidance in finding such approximations we discussed some exactly known properties of these functionals. We concluded that f_{xc} was a rather singular object. Whether or not this poses a problem for the development of better functionals remains to be seen.

Finally we discussed the derivation of the time-dependent Kohn–Sham equation from an action principle and concluded that, in order to avoid paradoxes, v -representability and boundary conditions require careful consideration. A well-defined action functional based on the Keldysh formalism was investigated in detail. With the Keldysh functional a previous paradox in TDDFT, related to the causality and symmetry properties of response functions, can be avoided. The formalism was illustrated with an exactly solvable example.

With respect to future developments it is fair to say that TDDFT is by now a well-established method within the field of quantum chemistry. Many response properties of molecules have been calculated accurately and at a much lower cost than other existing methods. However, there are also cases where TDDFT fails dramatically. This happens in the calculation of the polarizabilities and hyperpolarizabilities of long molecular chains.⁵⁸ It turns out that the simple LDA approximation is too local to notice the accumulation of charge at the ends of the chain.

There are close connections with density-functional theory of polarization and the problem may be solved by including a functional dependence on the polarization⁵⁹ or by orbital dependent functionals.⁶⁰

The use of TDDFT will certainly increase within solid state physics. There have been promising results on the calculation of dielectric functions²⁰ and spin waves.⁶¹ Since TDDFT calculations are computationally much faster than many-body perturbation theory methods, such as the ones based on the GW-approximation^{62–64} and Bethe–Salpeter equation,⁶⁵ we may speculate if TDDFT can compete in accuracy with these methods. In the calculation of dielectric functions it has been found that some peaks ascribed to excitonic effects are well-reproduced and in good agreement with Bethe–Salpeter results.²⁰ It may very well be that also bound excitons will be within reach of TDDFT.

There have been several extensions of density functional theory²⁶ that include currents, spin-densities, temperature and relativistic effects. These extended versions of DFT are easily cast into a linear response formalism. This means that within DFT several response functions, such as the spin–spin or current–current response functions, are accessible. Whether or not these quantities can be determined with sufficient accuracy will depend on the quality of approximate functionals. This will bring a new range of physical phenomena within reach of TDDFT. Based on recent experience with TDDFT it seems worthwhile to explore these new areas.

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Appendix A. The Sturm–Liouville Equation

In the proof of the extended Runge–Gross theorem of Sec. 2.5 extensive use is made of the Sturm–Liouville equation in the form of Eq. (72):

$$\nabla \cdot (n(\mathbf{r}) \nabla \omega(\mathbf{r})) = \zeta(\mathbf{r}). \quad (\text{A.1})$$

For our current discussion we will drop the time-argument of Eq. (72) as it only occurs as a parameter. We will now consider the conditions for which this equation has a unique solution for ω , given the density $n(\mathbf{r})$ and the inhomogeneous term

$\zeta(\mathbf{r})$. As a first step we note that this equation can be obtained as the variational Euler-Lagrange equation corresponding to minimization of the following functional

$$\Lambda[\omega] = \int d^3r \left[\frac{1}{2} n(\mathbf{r}) (\nabla \omega(\mathbf{r}))^2 + \zeta(\mathbf{r}) \omega(\mathbf{r}) \right], \quad (\text{A.2})$$

under the subsidiary boundary condition that $\omega(\mathbf{r}) \rightarrow 0$ if $|\mathbf{r}| \rightarrow \infty$. It is easily seen, for instance, that in the case $\zeta = 0$ this yields the unique solution $\omega = 0$. From this fact we can already conclude that if there is a solution to the Sturm–Liouville equation (A.1) that satisfies the boundary condition, then it is unique. If there were two solutions $\omega_1(\mathbf{r})$ and $\omega_2(\mathbf{r})$ then we would have

$$\nabla \cdot (n(\mathbf{r}) \nabla (\omega_1(\mathbf{r}) - \omega_2(\mathbf{r}))) = 0, \quad (\text{A.3})$$

from which we conclude, in combination with the boundary condition, that $\omega_1(\mathbf{r}) - \omega_2(\mathbf{r}) = 0$ and hence $\omega_1(\mathbf{r}) = \omega_2(\mathbf{r})$. Now we know that a solution which satisfies the boundary condition is either unique, or it does not exist. We further know that the density $n(\mathbf{r})$ is a physical density of a finite Coulombic system, and hence it decays exponentially for $|\mathbf{r}| \rightarrow \infty$. If there is a solution $\omega(\mathbf{r})$ with the required boundary condition that $\omega(\mathbf{r})$ be zero at infinity, then it follows immediately from the Sturm–Liouville equation (A.1) that $\zeta(\mathbf{r})$ must decay exponentially for $|\mathbf{r}| \rightarrow \infty$. In that case the integrals in the functional $\Lambda[\omega]$ of Eq. (A.2) are finite and the solution of the Sturm–Liouville equation corresponds to minimum of functional $\Lambda[\omega]$.

On the other hand, if $\zeta(\mathbf{r})$ decays slower than exponentially the Sturm–Liouville equation tells us that $\omega(\mathbf{r})$ must contain an exponentially growing term that cancels the exponential decay of the density $n(\mathbf{r})$. Because of this, $\omega(\mathbf{r})$ can not satisfy the boundary condition. It also means that for functions $\zeta(\mathbf{r})$ that do not decay exponentially the functional $\Lambda[\omega]$ can attain infinite values of arbitrary sign in which case it is clear that there is no variational minimum.

A solution that satisfies the boundary conditions does not exist in the case that $\zeta(\mathbf{r})$ decays slower than exponentially. If this is the case it means that the quantities that build up $\zeta(\mathbf{r})$, such as the stress-momentum tensor will decay slower than exponentially. This means in general that we are looking at a system for which the expectation value of the kinetic energy or potential are infinitely large. That we can find initial states with these unphysical properties has been shown in Ref. 32. We give a short account such a case in relation to the Sturm–Liouville equation.

We consider a simple one-particle system in one dimension. The particle evolves from an initial state $\psi_1(x)$ under the influence of a potential $v_1(xt)$ which is zero for $|x| \rightarrow \infty$. For this system the density is simply the square of the wavefunction $\phi_1(xt)$, i.e. $n(xt) = |\phi_1(xt)|^2$. For this one-dimensional system the stress-momentum tensor has only one-component with expectation value

$$T_{xx,1}(xt) = \left| \frac{d\phi_1(xt)}{dx} \right|^2 - \frac{1}{4} \frac{d^2 n(xt)}{dx^2}. \quad (\text{A.4})$$

Now we consider a second one-particle system with different initial state $\psi_2(x)$ and a different wavefunction $\phi_2(xt)$. Now we want that this second system has

identical density as our first system and therefore we have $|\phi_2(xt)|^2 = |\phi_1(xt)|^2$. The wavefunctions ϕ_1 and ϕ_2 can therefore only differ by a phase factor of the form

$$\phi_2(xt) = \phi_1(xt)e^{i\alpha(xt)}, \quad (\text{A.5})$$

where $\alpha(xt)$ is a real function. In particular we have for the initial states $\psi_2(x) = \psi_1(x)\exp(i\alpha(xt_0))$. From the continuity equation we then obtain the relation

$$0 = \frac{d}{dx}(j_2(xt) - j_1(xt)) = \frac{d}{dx} \left(n(xt) \frac{d\alpha(xt)}{dx} \right), \quad (\text{A.6})$$

where j_1 and j_2 are the currents of both systems. From the latter equation we obtain

$$\frac{d\alpha(xt)}{dx} = \frac{c(t)}{n(xt)}, \quad (\text{A.7})$$

where $c(t)$ is an arbitrary function of time. Now the potential of the system with wavefunction ϕ_1 goes to zero at infinity. This means that the force on the system

$$F_1(t) = - \int dx n(xt) \frac{dv_1(xt)}{dx} \quad (\text{A.8})$$

is finite and therefore also the momentum expectation value is finite. Since the momentum is given as

$$P_1(t) = \int dx j_1(xt), \quad (\text{A.9})$$

this can only be the case if $j_1(xt) \rightarrow 0$ for $|x| \rightarrow \infty$. We therefore see immediately that if $c(t)$ is not equal to zero that $j_2(xt)$ goes to a finite value at infinity. This means infinite momentum and infinite expectation value of the kinetic energy for system 2. It is also clear that then $\phi_2(xt)$ has a very pathological behavior as it will oscillate infinitely fast at infinity. It is exactly this pathological behavior that prevents the Sturm–Liouville equation of Eq. (72) of having a solution for ω . For our example we have $\omega(xt) = v_1(xt) - v_2(xt)$ and $\zeta(xt)$ is equal to

$$\zeta(xt) = \frac{d^2}{dx^2} (T_{xx,2}(xt) - T_{xx,1}(xt)), \quad (\text{A.10})$$

where $T_{xx,1}$ and $T_{xx,2}$ are the stress-momentum tensors of system 1 and 2. A simple calculation shows that Eq. (72) in our simple example reduces to

$$\frac{d}{dx} \left(n(xt) \frac{d\omega(xt)}{dx} \right) = \frac{d^2}{dx^2} \left(\frac{2c(t)j_1(xt)}{n(xt)} + \frac{c^2(t)}{n(xt)} \right) \quad (\text{A.11})$$

Now if $c(t) \neq 0$, then the right hand side of this equation grows exponentially for $|x| \rightarrow \infty$. In that case there is no solution for $\omega(xt)$ that vanishes at infinity. From our example it is clear that this is only due to unphysical infinities. The infinities can be avoided by requiring that $j_2(xt) \rightarrow 0$ for $|x| \rightarrow \infty$. In that case we obtain $c(t) = 0$ and the Sturm–Liouville equation has the unique solution $\omega(xt) = 0$.

It is interesting to note that the infinities in our example do not prevent a second potential $v_2(xt)$ to exist that yields the same density $n(xt)$. The infinities only

prevent the boundary conditions from being satisfied. In our pathological example there are infinitely many exponentially growing potentials that, for a given initial state, yield the correct density at all times.

In the previous example we considered a noninteracting system for which we saw that the solution of Eq. (A.1) was prevented due to the divergence of the stress-momentum tensor at infinity. This led to an infinite momentum and infinite kinetic energy. In the case of interacting particles we may wonder whether infinities due to the two-particle interaction may arise. It is readily seen that this is not the case. If we write out Eq. (72)

$$\begin{aligned} \nabla \cdot (n(\mathbf{r}t)\nabla(v_1(\mathbf{r}t) - v_2(\mathbf{r}t))) &= \sum_{i,k} \partial_i \partial_k (T_{ik,2}(\mathbf{r}t) - T_{ik,1}(\mathbf{r}t)) \\ &+ \sum_k \partial_k (W_{k,2}(\mathbf{r}t) - W_{k,1}(\mathbf{r}t)), \end{aligned} \quad (\text{A.12})$$

we see that the effects of the two-particle interaction is contained in the terms $W_{k,1}$ and $W_{k,2}$. These are of the form:

$$W_k(\mathbf{r}t) = \int d^3r' \Gamma(\mathbf{r}, \mathbf{r}', t) \partial_k w(|\mathbf{r} - \mathbf{r}'|), \quad (\text{A.13})$$

where Γ is the diagonal two-particle density matrix. We now use that $|\mathbf{r} - \mathbf{r}'| \approx |\mathbf{r}|$ for $|\mathbf{r}| \rightarrow \infty$ and use the following property

$$(N - 1)n(\mathbf{r}t) = \int d^3r' \Gamma(\mathbf{r}, \mathbf{r}', t), \quad (\text{A.14})$$

where N is the number of particles. This yields

$$W_k(\mathbf{r}t) \approx (N - 1)n(\mathbf{r}t) \frac{r_k}{|\mathbf{r}|} w'(|\mathbf{r}|), \quad (|\mathbf{r}| \rightarrow \infty) \quad (\text{A.15})$$

where w' is the derivative of w with respect to $|\mathbf{r}|$. We therefore see that $W_k(\mathbf{r}t)$ decays like the density and does not cause any infinities.

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